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PHYSICAL REVIEW.

A NEW RESPIRATION CALORIMETER AND EXPERIMENTS ON THE CONSERVATION OF ENERGY IN THE HUMAN BODY. I.

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I. INTRODUCTION.

THE purpose of this article is to describe a new respiration calorimeter and certain experiments made with it upon the conservation of energy in the human body. The apparatus has been devised and the methods of experimenting have been elaborated for use in inquiries upon the transformation of matter and energy in the living organism. This especial study is desirable for two purposes. One is the demonstration, so far as this may be possible, that the law of the conservation of energy holds in the living organism. The other is the practical application of this law in gaining more definite knowledge of the ways in which the body is nourished and of the values and uses of food. Preference has been given at the outset to the more theoretical problem of the conservation of energy, not only because of its profound scientific interest, but also because of its fundamental importance in the study of the laws of nutrition.

Development of the Investigations.

In the year 1892 the first steps were taken by the writers, at Wesleyan University, toward the development of a respiration calorimeter. The investigation was conducted under the patronage of the University, and in connection with the Storrs Experiment Station, of which Mr. Atwater is director. The progress of the work led to constantly increasing hopes of success, but at the same time showed more and more clearly the need of considerable amounts of labor and money in order to insure results at all commensurate with the importance of the inquiry. In 1894 provision was made by Act of Congress for an inquiry into the food and nutrition of the people of the United States. The responsibility for the inquiry was vested in the Secretary of Agriculture by whom it was assigned to the Director of the Office of Experiment Stations, and the immediate charge was placed in the hands of the Director of the Storrs Experiment Station as Special Agent of the Department of Agriculture. It was considered that a research, not only germane, but fundamental to such an inquiry might be appropriately aided from this fund, though the amount which could be utilized for this purpose was small. In 1895 the Legislature of Connecticut provided a special annual appropriation to be expended by the Storrs Experiment Station for food inquiries. The resources of the Station for this purpose were thus increased, and with the supplement from the general Government and with the aid from Wesleyan University and other sources, it has been possible greatly to enlarge the scope of this special investigation and to prosecute the work in a manner which would otherwise have been entirely out of the question.

The inquiry naturally divides itself into two parts. These have to do, as has already been stated, with the study of the law of the conservation of energy in the living organism on the one hand, and the study of the application of this law in the problems of animal nutrition on the other. That part of the inquiry which had to do with the establishment of the law of conservation of energy was undertaken jointly by the present authors. Mr. Rosa having recently retired from the investigation, the present article is intended to give an account of the development of the apparatus and methods and

some of the experiments with a human subject up to the time of his retirement. We wish to acknowledge our indebtedness throughout the entire period of the work to our associates, all of whom have entered into the work with enthusiasm. Mr. A. W. Smith, who has been engaged since 1894 in the physical side of the investigation, has rendered invaluable assistance in carrying out the experiments here described.

To Mr. O. S. Blakeslee, college mechanician of Wesleyan University, we desire to express our obligation for the meter pump, which was devised and made by him, and is briefly described in the following pages, and also for much valuable assistance in the construction of the apparatus.

A more detailed account of the apparatus, and especially of the experiments described in this article may be found in Bulletin 63 of the Office of Experiment Stations of the United States Department of Agriculture, from which the most of the illustrations of this article are taken.

METABOLISM OF MATTER AND ENERGY.

In so far as its material phenomena are concerned, life consists of transformations of matter and energy. To these transformations the term metabolism is commonly and appropriately applied. The processes of metabolism are thus of two definite and closely allied kinds, the metabolism of matter, in which the changes are chemical, and that of energy, in which the changes are physical. It is commonly assumed that these two classes of change in living organisms, animal and vegetable, conform to the two fundamental laws of the conservation of matter and the conservation of energy.

The main difficulty in demonstrating that the law of the conservation of energy holds in the living body is in measuring the transformations of energy which take place therein. To do this we must know how much energy the body receives, how much it gives out and how much it gains or loses of its accumulated store during a given time. In an experiment with a man, for instance, if we wish to demonstrate that the law of the conservation of energy obtains we must show that the income and outgo are equal. To show this equilibrium of energy we must determine the following quantities:

(1) the amount of potential energy the body receives as income in the food; (2) the energy it gives off (*a*) as potential energy in the unburned material which it excretes (in urine, feces, etc.), (*b*) as kinetic energy in the heat radiated from the body, and (*c*) as external muscular work done; and, finally, (3) the increase or decrease in the store of energy in the body during the experiment. If the body is warmer, or if it has a larger store of proteids or fat or glycogen or other substance containing potential energy at the end than at the beginning it has stored energy during the period. If, on the other hand, it is colder, or its store of substance containing potential energy is less at the end of the experiment than at the beginning, it has lost energy. This gain or loss of energy by the body itself, the increase or diminution of its store during the experimental period, must be taken into account if the experiment is to be accurate and reliable. Its exact quantitative determination is one of the most serious difficulties in such experiments.

In view of what was said above it might seem bold to attempt experiments with animals, or even with a man, in the expectation that any convincing proof of the application of this law could be obtained, and it might seem still more hazardous to assume that apparatus and methods of experimenting could be devised which should make it possible not only to demonstrate the law but to utilize it in general experiments upon the laws of nutrition. The task would not have been assumed in the present instance had not an attempt at least seemed warranted by a somewhat unusual combination of circumstances through which appliances and funds were available from several distinct sources, as already indicated. Nor is it at all surprising that, even with the unusual facilities thus brought together, a period of more than five years should have elapsed between the beginning of the actual work and the time when the first results were ripe for publication. It is not claimed that the results here reported suffice for a perfectly satisfactory verification of the law referred to. They are, however, in the judgment of the authors an important step in that direction.

II. APPARATUS AND METHODS.

OUTLINE OF APPARATUS AND PLAN OF EXPERIMENTS.

The name "respiration calorimeter" is suggested by the fact that it is essentially a respiration apparatus with appliances for calorimetric measurements. As a respiration apparatus it is similar in principle to that of Pettenkofer. As an instrument for measuring heat it is a constant temperature calorimeter, the heat being absorbed and carried away by a current of water as rapidly as it is generated in the chamber. The arrangements for the measurement of both the respiratory products and the heat given off from the body differ in important respects from those of any other apparatus with which we are familiar.

The essential features of the apparatus are:

1. A chamber in which the subject of the experiment lives, eats, drinks, sleeps and works during a period of several days and nights. The chamber is furnished with a folding chair, table and bed.

2. Arrangements for ventilation by a current of air which is drawn from out of doors, and passes through the chamber. The volume of this air current is measured and its temperature is so regulated as to be the same on entering the chamber as upon leaving. Samples for analysis taken before it enters and after it leaves the chamber give data showing the amount of carbon dioxide and water given off from the body through the lungs and skin.

3. Arrangements for passing food and drink into the chamber and removing the solid and liquid excreta. These materials are analyzed and give data for calculating the income and outgo of nitrogen; and also of sulphur, phosphorus, chlorine and metallic elements if these are determined. Taken in connection with the determinations of carbon dioxide and water in the respiratory products, they show the income and outgo of carbon and hydrogen. The analysis of the food, and solid and liquid excreta enable us also to determine the so-called digestibility of the food, *i. e.*, the proportions of nutrients actually made available.

4. Arrangements for measuring the heat given off from the body of the man in the chamber and the heat equivalent of the external, muscular work. The heat given off is carried away by a current of

cold water which passes through a series of pipes inside the chamber. By regulating the temperature of this water current as it enters, and also its rate of flow, it is possible to carry away the heat just as fast as it is generated, and thus maintain a constant temperature inside the chamber. The mass of the water and its increase of temperature are measured, thus determining the quantity of heat carried away.

In order that the heat taken up by the absorbers and carried out by the water current shall represent exactly the amount given off from the man's body or otherwise produced in the chamber, it is necessary to provide that there shall be no passage of heat through the walls, or rather that the small quantities that may pass in and out shall exactly counterbalance each other. Furthermore the ventilating current of air should leave the chamber at the same temperature as it enters, so that it shall carry out neither more nor less heat than it brings in, except that due to the greater quantity of water vapor in the air leaving the chamber over that in the air entering. This excess of water vapor is derived from the body of the subject, and the heat required to vaporize it must be added to the heat carried away by the current of water to obtain a measure of the total heat given off by the subject.

In the actual experiments the man remains for several days and nights (generally four days and five nights) in the chamber. The food and drink are passed in and the feces and urine removed at regular intervals. The diet is decided by the special question which is being studied, but is made agreeable to the subject of the experiment.

In some of the experiments the man had as little muscular exercise as practicable. In these so-called "rest experiments" no attempt was made to measure the muscular work. In others, so-called "work experiments," the amount of work done was measured by a specially devised ergometer, consisting of a stationary bicycle which was belted to a small dynamo. The electric current generated passed through an incandescent lamp inside the chamber where its energy was transformed into heat, the strength of the current and its voltage being determined by instruments outside the calorimeter. The heat derived from the muscular work done was thus

added to, and measured with, the heat given off from the body. The duration of the work and the amount of the electric energy generated gave data for the computation of the amount of muscular work performed.

The men who have served as subjects of the experiments have not found their sojourn in the chamber either inconvenient or disagreeable. The experiments are, however, very laborious, and require not only the services of trained observers day and night for the chemical and physical determinations, but also a considerable amount of painstaking work in preparing the food and attending to the numerous details, before, during and after the experiment.

ARRANGEMENTS OF THE APPARATUS.

A general idea of the apparatus can be had from Fig. 1, taken from a photograph. This gives a general view of the principal parts of the apparatus, which stands in a basement room of the Orange Judd Hall of Natural Science, at Wesleyan University. In the center is the large chamber, which is surrounded by a sheathing of wood. At the end of the chamber, on the right, is shown a door, which serves also as a window. At the right of the window and just below it are the arrangements for cooling and measuring the current of water which brings away the heat from the interior of the chamber. At the left, in front of the large brick pillar, is a table at which an observer sits to record the temperature of the interior of the apparatus and of the currents of air and water, the temperature being measured electrically. Behind the brick pillar is an ammonia refrigerating machine, not shown in the picture. Its purpose is to cool the solution of calcium chlorid which is contained in a large tank in the center foreground. This tank (Fig. 11) is inclosed within a double-walled wooden casing. The liquid ammonia is evaporated in the coiled iron pipe, shown in Fig. 11. The ventilating current of air, before it enters the chamber, is passed through the copper condenser, *A*, which is immersed in the calcium chlorid solution in the right-hand corner of this tank, and thus cooled to a temperature of from $-19°$ to $-20°$ C. At this very low temperature nearly all of the water is removed from the air, so that it enters the chamber quite dry. Just before entering at the right of the

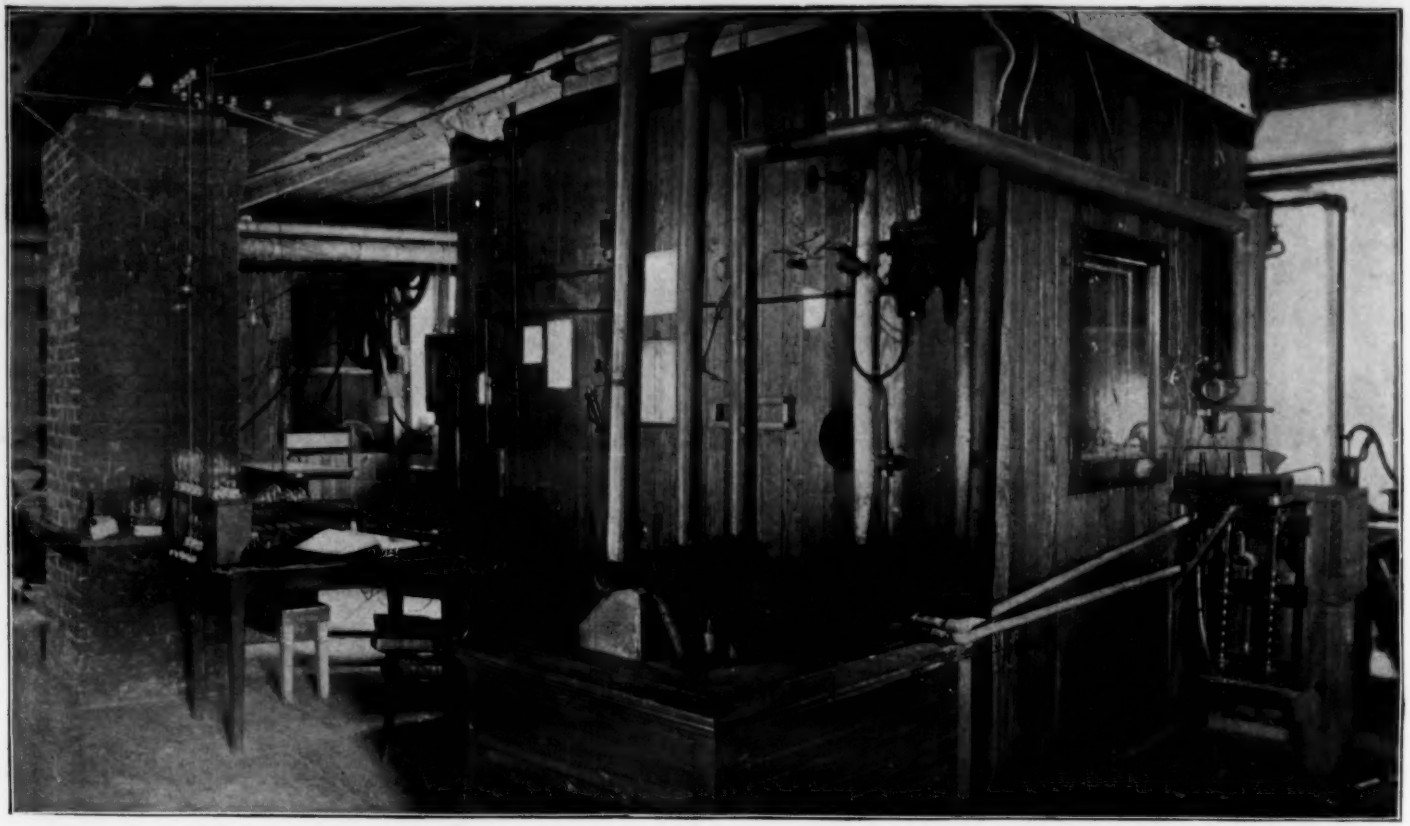


Fig. 1.

General view of the respiration calorimeter. Respiration chamber in center. Refrigerating tank in foreground. Water meter on the right. Observer's table on the left.

glass door it is warmed to the temperature of the interior of the chamber. On coming out it passes through a second condenser, consisting of a pair of copper cylinders, *B*, *C*, in the cold brine in the tank, and thus the larger part of the water which has been imparted to it by the respiration of the man inside the chamber is frozen and deposited. By means of valves contained in the valve boxes above the cylinders the air current may be diverted to a second pair of cooling cylinders, *D*, *E*. The first pair may then be removed and the deposited water determined by the increase in weight.

The window of the respiration chamber opens toward the east, so that the interior of the chamber is lighted from the two windows in the northeast corner of the room. At the west end of the room stands a 2-horsepower electric motor, belted to the driving pulley of a line shaft extending the entire length of the room. From this shaft power is taken to drive the ammonia refrigerating machine, the fans contained in the two fan boxes which circulate the air in the space surrounding the respiration chamber, and the meter pump which propels and measures the ventilating air current. A compression air pump is also driven from the shaft. This provides the compressed air which operates the valves of the meter pump. The air current passes from out of doors through a three-inch pipe into the refrigerating tank where the greater portion of its moisture is deposited, and thence to the respiration chamber (Fig. 5), after being warmed to the temperature of the latter. From the respiration chamber the air passes through the return pipe P_3 (Fig. 11) to the refrigerating tank, where its moisture is again deposited for the most part, and thence to the meter pump through P_4. Here the pump automatically records the volume of air and delivers every fiftieth cylinderful to the pans for analysis for carbon dioxid and residual moisture. Samples for analysis of the dried air of the pipes P_2, P_4 are drawn through quarter-inch brass pipes by the aspirators located at the south side of the room; and through similar pipes other samples are drawn off by aspirators in an adjoining room for duplicate analyses. The details of these operations will be given further on. On the north side of the pier near the middle of the room, and attached to the pier, is the galvanometer, used for meas-

uring electrically temperatures and differences of temperature; and on the observer's table are located Wheatstone bridges, keys and resistances used in the measurement and regulation of temperatures, as hereafter described. Tables and other appliances afford facilities for part of the chemical work done in connection with the experiment, but most of the chemical work is done in other portions of the building.

ARRANGEMENTS FOR PREVENTING A GAIN OR LOSS OF HEAT THROUGH THE WALLS OF THE CALORIMETER.

1. Construction of the Calorimeter.

The construction of the calorimeter is shown in horizontal section in Fig. 2. The inner chamber is practically an apartment with double walls of metal. The inner of the two metal walls is of sheet copper, and incloses a space 2.15 meters (7 feet) long, 1.92 meters (6 feet 4 inches) high, and 1.22 meters (4 feet) wide, the corners being rounded. Copper was chosen because it can be obtained in large sheets, can take a high polish and so the more fully reflect radiant energy, is a good conductor of heat and thereby tends to equalize local differences of temperature, and has a rather small specific heat. A window in one end, 70 centimeters high by 49 centimeters wide, serves also the purpose of a door. During an experiment, however, the door is sealed and a circular opening, *E*, which has tightly fitting caps *a*, *b*, both inside and outside, is used for communication with the interior. Outside is a box, *c*, filled with non-conducting material to prevent the passage of heat through *E*. The seams are soldered and the chamber is air-tight when the door and other openings are sealed. The outer metal wall is of zinc, which is less expensive than copper, and serves the purpose sufficiently well. Between the two walls is an air space, *A*, of 7.6 centimeters (3 inches). In this stands a wooden framework to which the two metal walls are securely attached.

In order to protect the calorimeter from the fluctuations of temperature of the basement room in which it stands it is enclosed within three concentric walls of wood. Through each of these is an opening corresponding to the window in the wall of the calo-

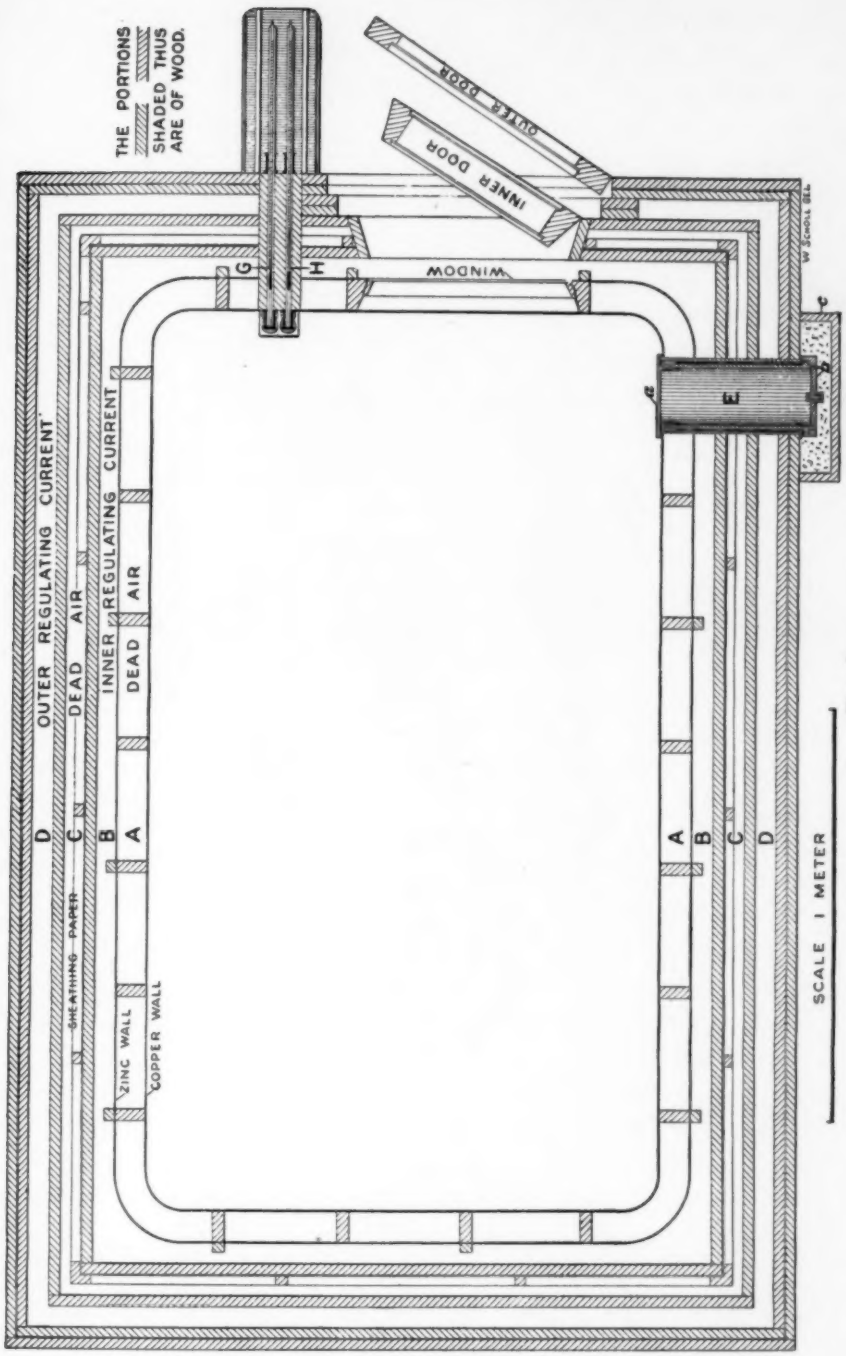


Fig. 2.
Horizontal section of the respiration calorimeter.

rimeter proper. These openings are closed by tightly fitting glass doors, hung on hinges.

Near these doors are shown the pipes through which the water enters and leaves the calorimeter. Its temperature on entering is measured by the mercury thermometer, *G*; and as it leaves, by a similar thermometer, *H*. Between the zinc wall and the innermost wooden wall is a 5-centimeter (2-inch) air space, *B*; between this wall and the next is a third air space, *C*, of 5 centimeters (2 inches); and, finally, between this wall and the outer one is a fourth air space, *D*, of 5 centimeters (2 inches). The wooden walls are made of matched pine, covered with building paper, and the outer one is double, with paper between. Of these four air spaces *A* and *C* are "dead" air spaces, while the air in the spaces *B* and *D* can be kept in constant circulation by means of rotary fans driven by power. Each of the air spaces *B* and *D* is continuous around the sides and over the top and bottom, and each communicates with its fan box in the rear by means of one passage extending from the top of the air space to the top of its fan box, and another from the bottom of the air space to the bottom of its fan box. Thus the air may be kept in constant circulation through these two air spaces and by heating or cooling this moving air the temperature of the corresponding space may be raised or lowered. We may also look upon the moving strata of air as shields, guarding the interior space occupied by the calorimeter from changes in temperature without. The walls at the top and bottom are constructed like those of the sides, but contain two flues for the regulating air currents. The air from the space *B* is drawn into the upper part of the bottom flue, and by means of the inner fan is driven into the lower part of the flue at the top. Openings along this flue allow the air to flow out over the top of the calorimeter, and thence down around the four sides to the bottom and so back to the fan again.

Similarly the air in the space *D* is kept in circulation by the fan in the outer fan box. The circulation in this space is in the opposite direction from that in *B*; that is, the air is taken from the top and driven in at the bottom. As the upper part of the room is usually much warmer than the floor, this arrangement for the outer circulating air tends to equalize the difference of temperature by drawing off the hot air from the top and driving it in at the bottom.

2. *The Thermo-electric Elements.*

In order to determine whether the inner or outer metal wall of the calorimeter is the warmer—that is, in order to know whether to heat or to cool the air space B—we use a large number of pairs (304) of thermo-electric junctions, distributed over the four sides, top and bottom of the calorimeter, one-half of the junctions (the iron-German-silver) being in close thermal contact with the copper wall and the other half (the German-silver-iron) with the zinc wall. One of these elements is shown in Fig. 3, where C_1 is a blank copper cartridge shell or cap, soldered to the copper wall, and maintaining the inclosed thermo-electric junction at the same temperature as the copper wall, and C_2 is a similar cap soldered to the zinc wall. There being copper leads connecting the several pairs, there are two junctions (copper-iron and German-silver-copper) in the outer cap; but these are thermo-electrically equivalent to the German-silver-

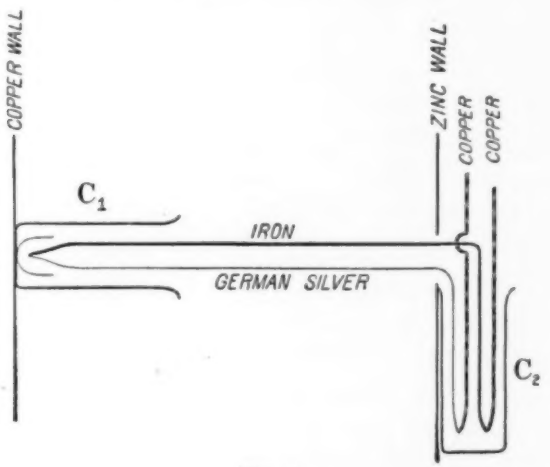


Fig. 3

Thermo-electric junctions. C_1 and C_2 are ordinary copper cartridge shells soldered to the copper and zinc walls respectively, and containing the junctions of the thermo-electric elements. Only one pair of junctions is shown in the figure, but there are really four such pairs in each group. The junctions are electrically insulated from the walls of the calorimeter, but in the best possible thermal contact.

iron junction. In reality there are four pairs of junctions in each group instead of a single pair as shown in the figure. These thermo-electric elements are made of silk-covered iron and German-

silver wire No. 20. They are all in series, and are joined to a sensitive D'Arsonval galvanometer. The galvanometer is quick and deadbeat, and readings may be taken rapidly. If the copper wall is on the whole warmer than the zinc, the electromotive forces due to the junctions in contact with it overpower those due to the junctions in contact with the zinc wall and a current flows through the galvanometer, proportional in amount to the difference of temperature of the walls, and produces a deflection to the right. It is then necessary to warm the space *B*, which raises the temperature of the zinc wall, and the deflection will be reduced. If the deflection is to the left, the space *B* is cooled until the deflection is zero. A deflection of 1 division on the scale represents a difference in temperature between copper and zinc of about 0.007° C. An experienced observer can ordinarily keep the deflection within one or two divisions, and by taking frequent readings at regular intervals the + and — deflections are separately summed up and made to cancel each other as the experiment proceeds, and hence no "cooling correction" is necessary.

Of course the deflection of the galvanometer is due to the algebraic sum of all the electromotive forces at the 304 pairs of elements. At some places the copper may be warmer and at other places colder than the zinc, and the galvanometer indicates the average difference. In order that this average may be the more reliable the elements have been spaced as nearly uniformly as possible over the entire surface. There are 76 groups of elements of 4 pairs each: Of these 76 groups 11 are on the top, 11 on the bottom, 22 on the upper part of the four sides (over two-fifths of the whole area), and 32 on the lower part of the four sides (covering the remaining three-fifths of the area). Thus the elements are joined up in four sections, designated respectively as top, upper, lower, and bottom, and each section can be joined to the galvanometer separately. In practice, therefore, we can determine whether to heat or cool any of the four sections, top, upper, lower or bottom, in order that the deflection shall always be small for each section, and that the total deflection for all shall be zero. This secures a more perfect balance than could be had if only the total deflection were zero; for then an appreciable quantity of heat

might be flowing in at the top and out at the bottom and the two quantities not exactly balancing each other.

There are 26 pairs of thermo-electric elements set in the wooden wall between the air spaces *B* and *D*, one set of junctions extending into the air space *B* and the other into *D*. These elements indicate the difference of temperature between *B* and *D*, and indicate when *D* must be heated or cooled to keep it nearly at the temperature of *B*.

3. *Heating and Cooling Appliances.*

In order to be able to heat or to cool any of the four sections of the air space *B* separately, a system of German-silver wires for heating and of iron pipes for cooling are arranged in this space, between the inner wooden wall and the zinc wall. German-silver wire No. 30 was stretched horizontally around the calorimeter, being supported and insulated by passing it through glass tubes set into vertical wooden strips which are attached to the zinc wall. The wire was divided into four sections corresponding to the four sections of the thermo-electric elements and the ends brought out so that an electric current could be passed through any of them at will, the strength of the current being regulated by variable resistances. In a similar manner ¼-inch (6-millimeter) iron pipes are arranged in four sections so that by opening a valve water from the city service can be passed through any of the pipes, to cool the surrounding space; when the water is shut off, a vent in each of the valves allows the pipes to drain. When only slight cooling is needed, the water may be allowed to flow only a few seconds at a time. In this manner the temperature of the air space can be perfectly controlled, and when the temperature within the calorimeter remains constant, as when heat is being generated at a uniform rate, the deflection can usually be kept within 1 division, which means an average difference of temperature between copper and zinc of less than 0.01°C.

Inasmuch as the temperature of the room is always lower near the floor than near the ceiling, the air circulating through the space *D* is warmed by passing over electric lamps or through a pipe heated by a Bunsen burner and made to enter at the bottom of the calorimeter. This tends to equalize the temperature between the

top and the bottom, and guided by the indications of the second set of thermo-electric junctions, the air in *D* is kept nearly at the temperature of that in *B*. Thus the space *B* is perfectly protected from changes of temperature without, and it is possible to keep its temperature almost the same as that within the chamber.

4. *The Observer's Table.*

The terminals of the thermo-electric circuits and of the galvanometer are brought to the observer's table (Fig. 4). The galvanometer stands on a shelf attached to a brick pier, about 2 meters beyond the table, and the galvanometer scale is directly over the table, being also attached to the pier. A 4-point switch, *N*, joins the galvanometer to the several thermo-electric circuits in succession. If the key is on the first point, the thermo-electric circuit of the copper-zinc walls, designated as No. 1, is joined to the galvanometer, and the deflection indicates their difference in temperature, as already explained. An auxiliary switch, *M*, throws into the circuit any of the four sections separately, or all together when desired.

The 26 pairs of thermo-electric elements, designated as circuit No. 2, set in the wooden wall between the spaces *B* and *D*, are joined in series, and the terminals are brought out to the switch *N*, and joined to the galvanometer when the key is on the second contact. The galvanometer then indicates whether the space *D* is warmer or colder than *B*, and thus shows whether to heat or to cool the air flowing through it. If the temperature of the room is not very different from that of the calorimeter it is not necessary to heat or cool the air in *D*. But if the room is much colder than the respiration chamber, as is often the case at night when there is no steam in the radiators in the room, then by heating the air of *D* before it enters at the bottom it protects the space *B* from outside influence. The temperature of the room not infrequently falls in winter to 15° or 13°C., while that of the respiration chamber is maintained constant, usually at about 22°C.

When the key is on the third contact the galvanometer is short-circuited, and when on the fourth the thermo-electric junctions, designated as circuit No. 4, in the ventilating air current, hereafter to be described, are joined to the galvanometer.

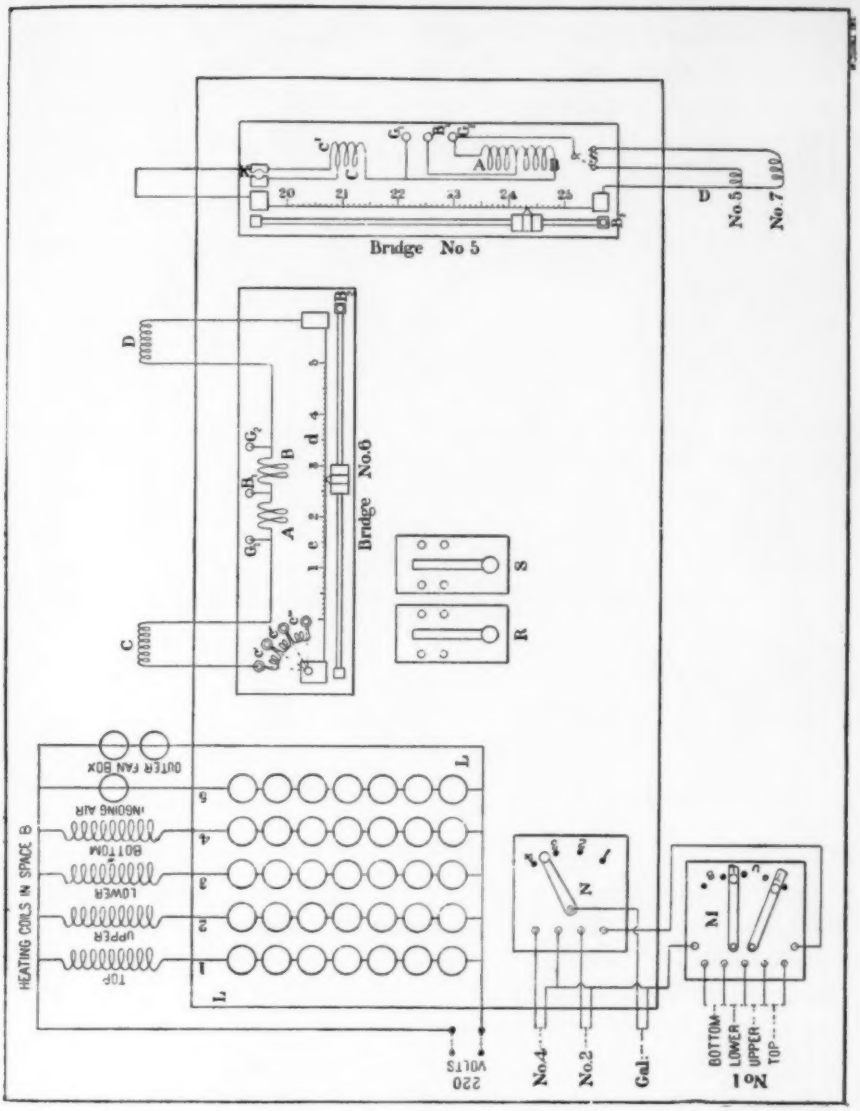


Fig. 4.

Diagram of electric apparatus at the observer's table. Bridge No. 5 is a special Wheatstone bridge used in measuring the temperature of the respiration chamber. Bridge No. 6 is used to measure the difference of temperature of the ingoing and outcoming water. *R*, *S* are two electric keys. *L*, *L* is a bank of incandescent electric lamps used as variable resistance. *M*, *N* are two multiple switches.

A bank of incandescent lamps, *LL*, is divided into five groups of 7 lamps each. Each of four groups is in series with one section of the German-silver heating coils already referred to, and which are wound around the calorimeter in the air space *B*. For example, the first section is in series with that section of the coil distributed over the top of the calorimeter, and the current is regulated by varying the number of lamps in series. Any one or more lamps can be cut out of circuit by a short-circuiting key. The lamps have different resistances, and by suitable combinations any desired current may be obtained, the source of current being the 220-volt-power circuit from which the electric motor is driven.

The fifth section of lamps is in series with an incandescent lamp placed in the pipe through which the ventilating current of air enters the respiration chamber, and by regulating the current through it, the temperature of the air as it enters is maintained the same as that of the air leaving.

Bridge No. 6 is a Wheatstone bridge, by means of which the difference of temperature of the stream of water as it enters and leaves the calorimeter is measured, and bridge No. 5 is a similar Wheatstone bridge for determining the temperature of the respiration chamber. These bridges will be described later.

APPARATUS AND METHOD FOR MEASURING THE HEAT.

1. *The Water System.*

Having arranged the calorimeter so that no heat can escape or enter through its walls, it remains to carry away and measure the heat generated. This is done by a stream of water flowing through a copper "absorber" (*HH*, Fig. 5). A copper pipe of 6 millimeters (¼ inch) bore was bent into a rectangle 90 centimeters by 182 centimeters (3 feet by 6 feet). In order to increase the absorbing area of the pipe, one thousand disks, *II*, 5 centimeters (2 inches) in diameter and with a 1 centimeter (⅜ inch) hole in the center, stamped out of sheet copper, were slipped over the pipe like beads on a string, and soldered 6 millimeters (¼ inch) apart. The pipe and disks were then painted black. This absorber is suspended about 25 centimeters (10 inches) below the ceiling of the calorimeter,

and 15 centimeters (6 inches) from the sides and ends. Water enters the calorimeter from the coolers through a pipe, *E* (Figs. 5

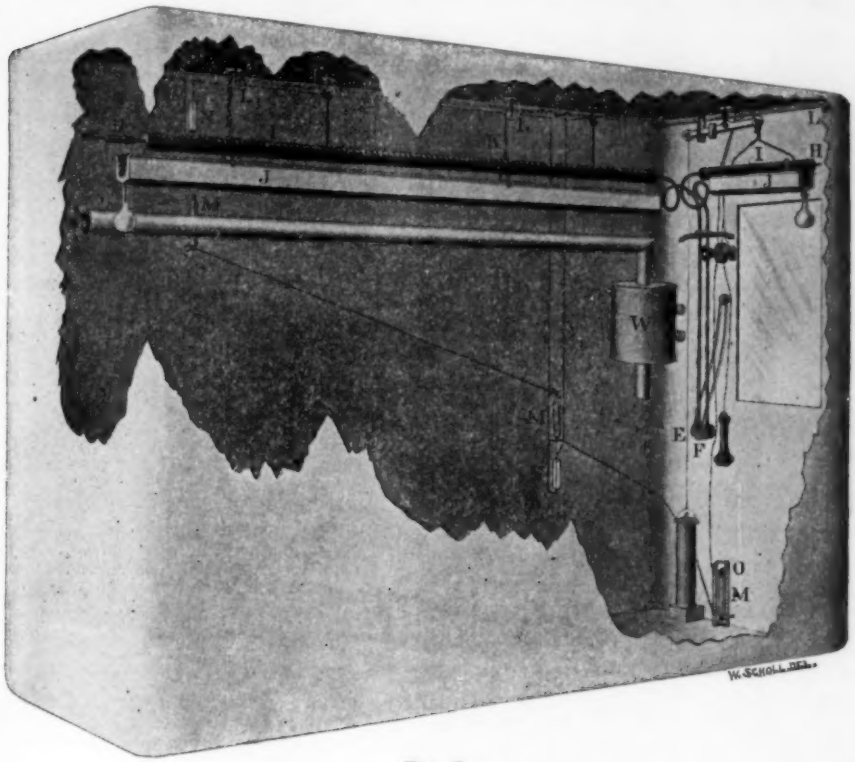


Fig. 5.

Interior of respiration chamber. This is the view which would be secured by breaking away a portion of one side and end of the interior copper wall of the respiration chamber. The ventilating air enters the chamber through the bottom of *W*, leaving from the rear of the chamber through the long tube connected with the upper end of *W*. The copper tubes *H*, *H*, strung with copper disks, *I*, *I*, constitute the absorbers through which flows the water current which carries away the heat generated in the chamber. *J*, *J* are the copper troughs for collecting the drip from the absorbers. *M*, *M*, *M* are the electrical thermometers which show the temperature of the air in the chamber; *N*, *N*, those which show the temperature of the copper wall.

and 6), containing a mercury thermometer, *G*, and after flowing through the absorber leaves through a second pipe, *F*, near to and parallel with the first, containing a second thermometer, *H*. These two water pipes pass through holes in a cylindrical block of wood. The bulbs of the thermometers are at points, *g*, *h*, midway between

the zinc and the copper walls. Hence one gives the temperature of the water just as it enters the respiration chamber and the other its temperature as it leaves. The thermometers are 60 centimeters (24 inches) in length, and are graduated from 0° to 30° C., in

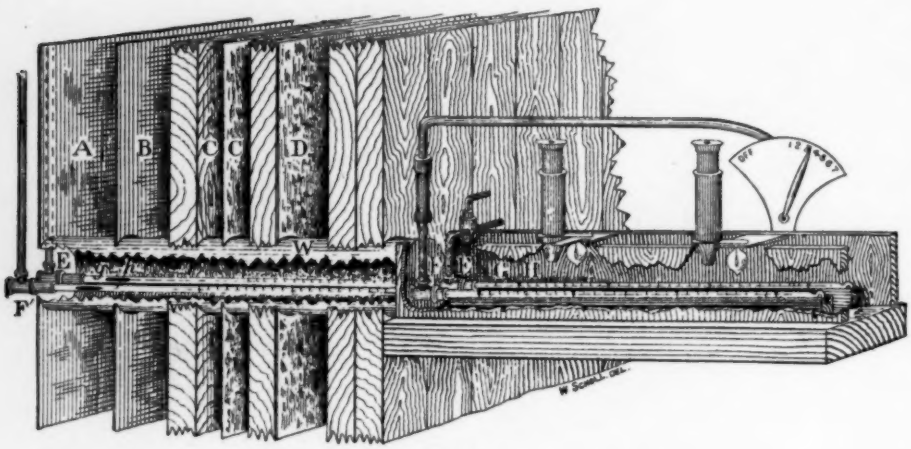


Fig. 6.

Section through walls of the calorimeter showing thermometers. *A* is the copper and *B* the zinc wall of the calorimeter chamber. *C* and *D* are the inclosing walls of wood and paper. The long thermometers *G*, *H*, extend into the two pipes *E*, *F*, through which the current of water enters and leaves the calorimeter. Readings are taken by means of the microscopes, the scale being illuminated by small electric lamps. The rate of flow of water is regulated by a valve with an index moving over a graduated scale.

twentieths of a degree, and read to hundredths of a degree. They have been carefully compared with our standards. These thermometers are read by microscopes mounted as shown in Fig. 6, the thread of mercury bearing illuminated by small electric lamps. Their difference of temperature gives a measure of the heat absorbed within the calorimeter per gram of water.

In order to regulate the temperature of the ingoing water, and especially to have it as low as required, it is passed through a cooler. This consists of a pair of closed copper cylinders submerged in a bath of cold calcium chlorid. The temperature of this bath is kept at the desired point by pumping in cold calcium chlorid solution from the large refrigerating tank as often as necessary. The water to be cooled enters the first cooler, being carried to the

bottom where the warm water prevents the formation of ice. This water being partially cooled enters the second cooler, being carried to the bottom as in the first one. Here it is cooled still further before going to the absorbers. By this means the ingoing water can be brought as low as 2° C. if desired, and any higher temperature can be obtained either by varying the temperature of the bath or by mixing the cold water with warmer taken directly from the supply. At the top of the room is a tank which is kept full and overflowing by a stream of water from the city service. From this tank is taken the water which flows through the absorbers. Having thus a constant head, the rate of flow of water through the absorbing pipes is uniform. A regulating valve with a pointer moving over a graduated arc (Fig. 6) enables one to vary the rate of flow within wide limits.

2. *The Water Meter.*

The water is received in a special form of water meter (Fig. 7), having a capacity of 10 kilograms. The water which has flowed through the absorbers runs into the small cup, *A*, which is divided by a vertical partition through the center and reaching from the bottom about half-way to the top. On either side of this partition are small tubes leading from the bottom of the cup, *A*, to the cylinders, *B* and *C*. When the water running into *A* falls on one side of the partition it will run down the tube to the corresponding cylinder, which will be filling up. As the level of the water rises it will finally be as high as the top of the partition in the little cup, *A*, when no more water will enter, but will overflow and run into the other cylinder. The first cylinder now contains just 10 kilograms of water.

In the narrow neck of the cylinder is a float, *F*, in the form of a test tube. This is hung from the end of a spring, and as the rising water lifts the float the spring comes in contact with the point *H*, and closes the circuit of an electric alarm bell which continues to ring until the siphon, *S*, is started and the cylinder begins to empty. After the siphon is started it will draw all the water from the cylinder down to a certain level without any further attention. The stream of water is diverted to the other side of the cup, *A*, by the

operator before the siphon is started. Record is made at the instant the meter is filled and the interval between successive records

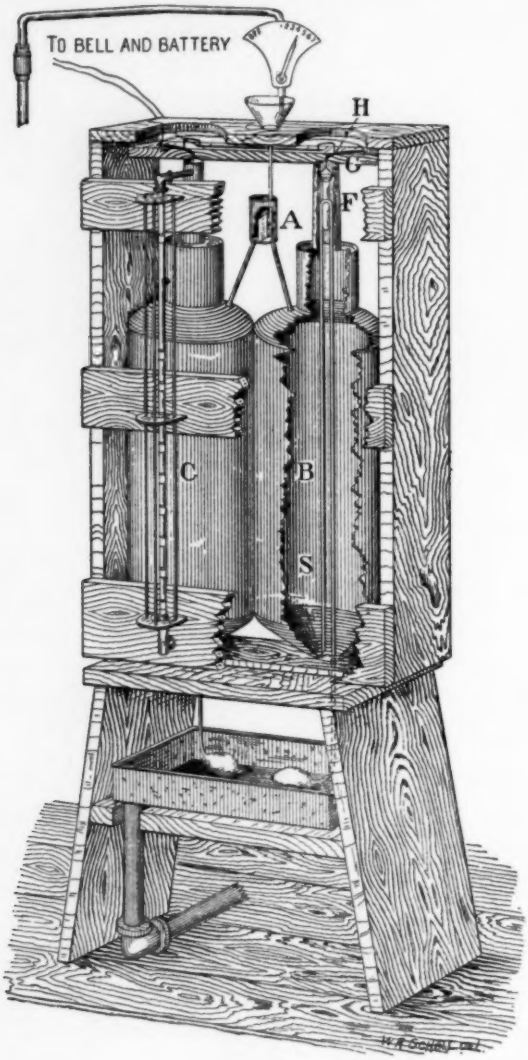


Fig. 7.

Water meter. The stream of water which carries away the heat generated in the respiration chamber flows into one of the cylinders *B*, *C*, until it is filled, when the stream is diverted automatically by the apparatus *A*, to the other cylinder. The first is emptied by means of the siphon *S*. The siphon is operated by the attendant whose attention is called by an electric bell which begins to ring as soon as the cylinder is filled, and continues ringing until the siphon is started.

gives the period for the corresponding 10 kilograms of water. Thus the product of the average difference of temperature between the ingoing and outgoing water by 10 gives the number of calories of heat brought away during the given period.

3. *Determining the Increase of Temperature of the Water.*

As a check upon the thermometer readings, and in order to avoid too frequent readings of the thermometers, two coils of copper wire are sealed in thin copper tubes and inserted in the water pipes near the bulbs of the thermometers. They are joined to two comparison coils on the slide-wire Wheatstone bridge, No. 6 (Fig. 4), graduated so that readings on the scale give differences of temperature of the water in the pipes, 1 millimeter being 0.01° C. Readings on this bridge are usually taken every two minutes during an experiment, and careful readings on the mercury thermometers are taken occasionally for calibration purposes. This bridge is equivalent to what is generally known as a platinum thermometer, but inasmuch as copper coils are used instead of platinum, it is here called a "copper thermometer." The resistance of copper increases with its temperature, and hence the difference of temperature of two coils of wire may be accurately measured by determining their resistances.

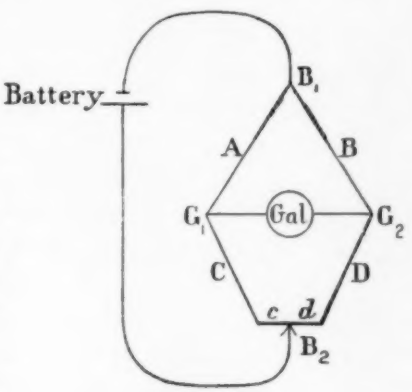


Fig. 8.

Diagram illustrating use of copper thermometer. This is a Wheatstone bridge in which A and B are two equal comparison coils; C is a fixed resistance; D is the resistance coil in the calorimeter, and c and d are the two parts of the straight wire on the bridges shown in Plate VI.

The principle employed for the measurement of these resistances is, as just stated, that of the Wheatstone bridge, illustrated in Fig. 8. The four arms are A, B, $C + c$, $D + d$. The battery is joinedat B_1 and B_2, the galvanometer at G_1 and G_2. If A and B represent the proportional arms of the bridge, which are here equal, C and D the two copper coils in the water

pipes, and $c + d$ the slide wire of the bridge, then for no current through the galvanometer the following proportions must be true :

$$A : B : : C + c : D + d.$$

Suppose now the coil D is warmed so that its resistance is increased. To keep the bridge still balanced, B_2 must be moved along the slide-wire reducing d, and, at the same time, increasing c, until the bridge is again balanced. By properly graduating the slide-wire scale the position of B_2 will show directly the difference in temperature between the coils C and D; and these coils of fine insulated copper wire, inclosed in very thin copper tubes, quickly take up the temperature of the water by which they are surrounded.

Referring now to Fig. 4, the connection of bridge No. 6 will be readily seen. The parts are lettered the same as in Fig. 8. In addition are the small coils c', c'', c'''. The length of the bridge wire corresponds to a difference of temperature of 5° in the coils C, D. If the difference increases above this, the coil c' is added to C, so that the slider instead of being at "5" will be at "0," and then differences of temperature between 5° C. and 10° C. can be measured. In the same way, when the difference reaches 10° C., c'' is added to $C + c'$, and "0" then corresponds to 10° C. The connections are made and changed by means of a heavy link dipping into mercury cups. The scale is 500 millimeters in length, and hence the position of the slider can easily be read off in hundredths of a degree.

The rate at which heat is taken up by the absorbers depends upon their temperature as compared with that of the surrounding space, and the freedom of circulation of air around them. Three methods are employed to diminish this rate below the maximum. First, the water may be allowed to enter at a higher temperature than the minimum of 2° C.; second, the water may be made to flow slowly through the absorbers so that its average temperature is higher; and third, shields may be put around the absorbers. Deep copper troughs, J, J, hang under the absorbers (see Fig. 5), one on each side and one on each end. The side troughs or shields can be operated from without by means of cords passing over pulleys, L, L, which are wound up by rods reaching through the side of the calorimeter. Raising a shield around a portion of the absorber im-

pedes the circulation of the air, the colder air within the shield being able to escape only by rising and flowing over the sides. As these shields can be raised to any desired point, and the temperature and rate of flow of the entering water can be regulated at will, any desired rate of absorption from 1 to 250 calories per hour, its maximum rate, can be realized.

4. *Determining the Temperature of the Calorimeter.*

In order to measure not only the total amount of heat evolved by the subject, but also the rate at any and all times, it is necessary to keep the interior temperature of the calorimeter very nearly constant, and also to measure the small changes in temperature which may occur. For this purpose we have mounted six coils of No. 32 copper wire near the walls of the chamber, connected them in series with one another and joined them to a slide-wire bridge (No. 5, Fig. 4), outside, so graduated as to read off the temperatures directly in degrees Centigrade, 1° extending over a hundred millimeters on the scale. Thus the temperature is read to the hundredth of a degree. This bridge is similar to No. 6. *A* and *B* are the proportional arms of the bridge, here equal to each other, *C* is the comparison coil mounted on the bridge. The wire of coil *C* (as well as both bridge wires) was kindly furnished by the Weston Electric Instrument Company, and has a zero temperature coefficient, so that its resistance is constant. Hence the position of the slider is changed only when the temperature of the copper thermometers, *D*, varies. At *K* is a switch for short circuiting the small coil *c'*. When this is closed the scale reads from 17° C. to 22° C.; when open, from 20° C. to 25° C. The copper coil *D*, which forms the fourth arm of the Wheatstone Bridge, is subdivided into six separate coils. Two of these are mounted on each side of the chamber and one on each end, each being at a different height, *M*, *M*, *M* (Fig. 5). Thus they indicate a fair average temperature. These coils are wound on light wooden frames and are covered by a perforated brass tube. They are thoroughly insulated from the copper wall, and further protected from injury by guards, *O* (Fig. 5). They are very sensitive to slight changes in the temperature of the air.

A second set of similar coils is enclosed in copper boxes and at-

tached in close thermal contact to the copper walls. They may be joined to the same bridge by a key, *S*, and indicate the temperature of the copper walls. These copper coils, with their slide-wire bridge, we call the "copper thermometers." A mercury thermometer passes through the wooden and zinc walls, and its bulb lies in a copper pocket which is soldered to the copper wall. This gives the temperature of the copper at that place, and its readings are compared with the "copper thermometer" readings.

THE VENTILATING AIR CURRENT.

1. *Measuring and Regulating the Temperature of the Ingoing Air.*

The temperature of the out-coming air will be the same as that inside the chamber. If the in-going air can be kept at the same

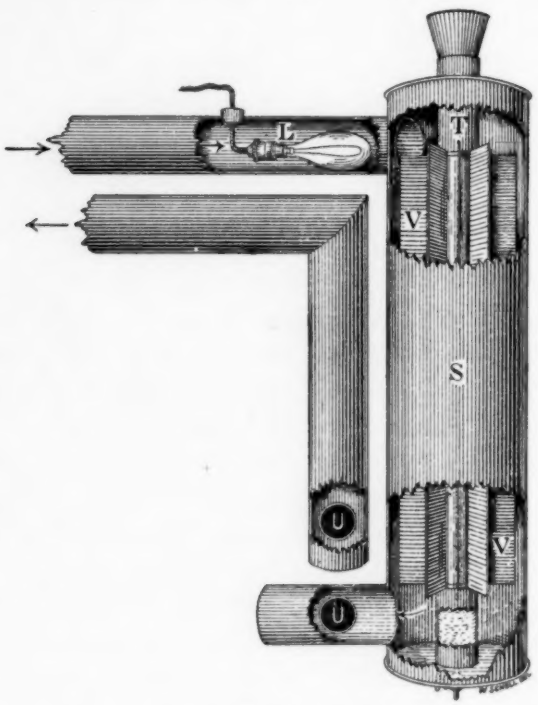


Fig. 9.

Air temperature regulator. The ventilating current of air passes through this regulator on its way to the calorimeter and the temperature is raised by the lamp, *L*, or lowered by water contained in the cylinder, *T*, as may be necessary to make it the same as the temperature of the air escaping through the exit pipe, *U*.

temperature there will be no gain or loss of heat due to the circulation of the air.

The in-going air passes through the "regulator" before entering the chamber. This regulator, shown in Fig. 9, is a copper cylinder 76 centimeters (30 inches) long and 18 centimeters (7 inches) in diameter. Within this is another cylinder 5 centimeters (2 inches) in diameter extending through the ends of the outer one. On the outside of this small cylinder are soldered eight vanes, *V*, which reach nearly to the outside wall, thus increasing the effective area of the cylinder, which is filled with water to increase its capacity for heat. The air comes to the regulator a few degrees too cold, and it is warmed by an incandescent lamp *L*, placed in the pipe. The current in the lamp is varied to give the required amount of heat. After passing over the lamp and being warmed to about the desired

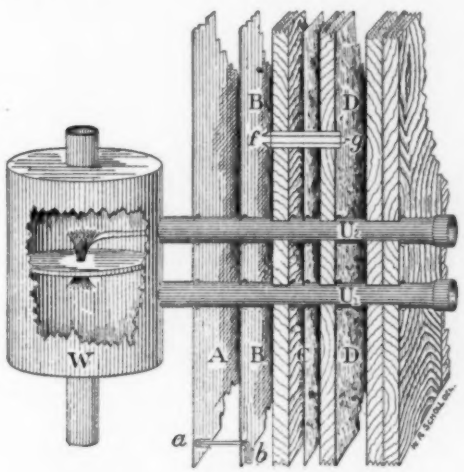


Fig. 10.

"Vestibule." The object of this apparatus is to facilitate the comparing of the temperature of the in-coming and out-going ventilating current of air. The air enters the lower part of the vestibule through the lower pipe U_1, and leaves the upper part through U_2. The thermo-electric junctions set in the partition between the upper and lower parts of the vestibule indicate any difference of temperature between the entering air and that which is about to flow out.

temperature the air enters the regulator *S*, where it attains its final uniform temperature. If it enters a little warmer it will impart its surplus heat to the water in the small cylinder, *T*, while if it enters

slightly cooler it will receive heat from the same source. Thus it will enter the chamber through the tube, U, at a nearly constant temperature. This regulator of large capacity for heat steadies the temperature of the air current as a massive fly wheel of an engine steadies its speed.

Within the chamber is the "vestibule" (Fig. 10), through which pass the currents of in-going and out-coming air. This is a double-walled copper chamber, divided into two portions by a double-walled partition. The out-coming air enters the top and passes out through the tube, U_2. This space will then have the temperature of the out-coming air. In the same way the in-going air enters through the tube, U_1, and leaves at the bottom. The lower space is then at the temperature of the in-going air. Extending through the partition on either side are twenty-four pairs of iron-German-silver thermo-electric couples. These are connected to the galvanometer through point 4 of switch N (Fig. 4), and if there is any difference of temperature between the air in the two spaces it will cause a deflection of the galvanometer. If this shows that the in-going air is cooler than the outcoming, the current in the lamp (Fig. 9) is increased. If the air should require to be cooled, as rarely occurs, this may be effected by drawing off a portion of the water and replacing it by colder water.

2. *Refrigerating Apparatus.*

The refrigerating tank is shown in Fig. 11. Liquid ammonia is supplied to the tank through the iron pipe marked P_5 from an ammonia machine in another part of the room. This liquid ammonia, initially at high pressure, passes through a reducing valve and flows into the coil of iron pipe shown in the figure. Here it evaporates, as it flows around the coil, as rapidly as heat can be absorbed from the solution of calcium chlorid which fills the tank. The temperature of this solution is thus reduced to about $-18°$ or $-20°$C. The coil of pipe through which the ammonia passes consists of 88 meters (287 feet) of 2.5 centimeters (1 inch) extra-heavy pipe electrically welded so as to form one continuous tube. There are two sets of air refrigerators or "freezers" in the tank. The first is marked A, and is made of sheet copper. It consists practically of

two large U tubes of copper immersed in the brine and connected by horizontal elbows. Copper vanes attached to the walls of the freezer increase the cooling surface. The air enters the pipe P_1 from

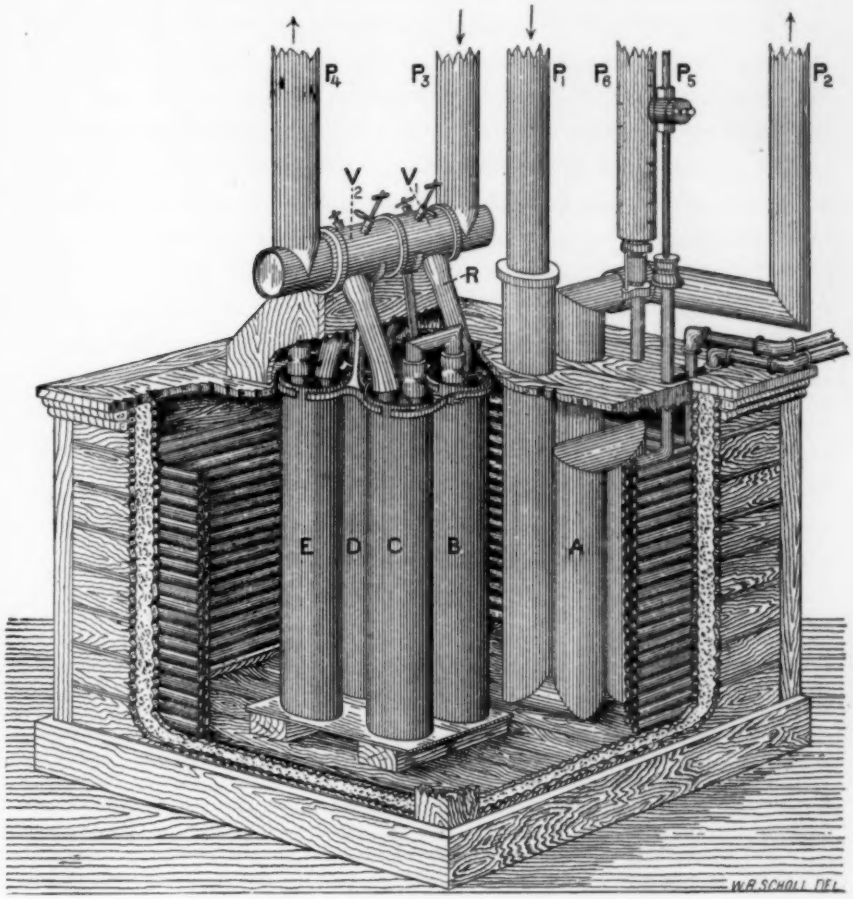


Fig. 11.

Refrigerating apparatus. The chief object of this is to remove the greater portion of the moisture from the ventilating current of air before it enters and after it leaves the respiration chamber. For this purpose the air is passed through copper cylinders, "coolers," *A*, *E*, immersed in brine (of calcium chlorid) which is cooled to a temperature of — 18° to — 20° C. by aid of ammonia expanding in the coiled pipe seen against the sides of the tank in the figure. The air flows through the cooler, *A*, on its way to the respiration chamber, and through *B*, and *C* or *D* and *E* on its way from the chamber to the pumps. The valves, V_1 and V_2, are used to direct the outcoming air current from one pair of cylinders to the other.

out-of-doors laden with more or less moisture. Reaching the freezer A its temperature is quickly lowered nearly to that of the surrounding brine and nearly all of its moisture is deposited upon the inner walls of the freezer. The air leaving the freezer A, passes along the pipe P_2 to the calorimeter, being warmed to the temperature of the room before reaching the chamber. Its moisture content as it enters the calorimeter is quite small and uniform.

Returning from the calorimeter laden with water vapor, the air passes through the second system of refrigerators or freezers, in which the greater portion of this moisture is condensed. But in order to be able to collect and measure the deposited moisture for any given period, this system of freezers is differently constructed from that used for the in-coming air. Four cylindrical brass vessels are clamped together, as shown in the figure, and fitting closely inside them are four cylinders or freezers made of sheet copper. Each of these is about 57 centimeters (22.5 inches) long and 12 centimeters (4.75 inches) in diameter, and is divided vertically by a partition which extends from the top nearly to the bottom. The air enters through a tube in the top, flows down to the bottom, and, rising on the other side of the partition, passes by means of a double-elbow connection to a second freezer, where the larger portion of the water not removed by the first freezer is condensed. In order to give a maximum cooling surface, vanes of sheet copper are soldered to the interior surface of the cylinders extending radially to within a short distance of the middle partition. The space between the inner cylinder or freezer and the outer protecting jacket is filled with alcohol, in order to insure a freer passage of heat from the air current to the cooling brine. The freezers are removed and weighed at intervals, generally of six hours. In order that this may be done conveniently and without interfering with the regular flow of the air current two pairs of cylinders are used and a valve box is so arranged that the air current can be easily diverted from one pair to the other. This consists of two pieces of brass pipe, 10 centimeters (4 inches) in diameter, placed end to end. The adjoining ends are separated by a disk of vulcanized fiber, which serves to prevent the passage of both air and heat from one tube to the other, while the open ends are connected to the air pipes P_3 and P_4 (Fig.

11). The valve box is provided with four lateral apertures, fitted with collars and rubber couplings, to connect it with the freezers. An arrangement is made for conveniently opening and closing these apertures by rubber stoppers, which are held by brass rods reaching through the walls of the valve box and worked from the outside. Two openings on one side are connected with one pair of freezers, while the two on the other side are closed. When it is desired to change the freezers the current is diverted from one pair to the other by means of these valves. The first pair of freezers is then taken out, warmed, dried and weighed; the increase in weight during the period gives the moisture condensed from the air current.

3. *The Blakeslee Meter Pump.*

Two forms of apparatus have been used for maintaining the air current and measuring its volume. The first consisted of an exhausting air pump used in connection with a special form of gas meter made by Elster in Berlin. With this we did a large amount of preliminary work, but were unable to make measurements of air volumes as accurately as we desired.

Aspirators containing 150 liters each were employed at the outset and are still used for taking samples of air for analysis. Measurements with these aspirators have been found quite accurate. But a much more satisfactory arrangement, and one which serves the threefold purpose of maintaining the air current, measuring its volume, and delivering aliquot samples of convenient volumes for analyses is an apparatus designed and constructed by Mr. O. S. Blakeslee and appropriately designated by him as a "meter pump." This is shown in Fig. 12. The essential parts for maintaining the air current and measuring its volume are cylinders of steel. There are two pumps, which work synchronously. Three steel cylinders are employed for each pump. Two of them are fixed concentrically, with a narrow annular space between them. This space is nearly filled with mercury and in it plays the third cylinder, its lower portion being immersed in the mercury. This moving cylinder is closed at the top and is raised and lowered by a walking beam. The length of the stroke of the cylinder is uniform, and the volume of air delivered at each stroke is constant. The temperature of the

pump is kept practically constant, so that the mass of air of each stroke is constant. Like the moving cylinder, the inner cylinder is also covered at the top, but through this cover are two circular apertures, opened and closed alternately by an automatic valve.

The pump is driven by a belt on the large pulley, shown back of the walking beam, from a countershaft overhead. The speed is reduced by gearing, so that the face wheel in front rotates about ten times a minute. On the same shaft with the walking beam is a sleeve with a projecting arm, which is nearly hidden behind a portion of the walking beam. The end of this arm is attached to the face wheel by a connecting rod, as shown in the figure. This conveys an oscillatory motion to the sleeve, which is transmitted to the walking beam by the straight steel springs, the ends of which are connected about the middle of the arcs.

The moving cylinders are suspended from the circular ends of the walking beam by flexible steel straps, each of which is wrapped around the end of the beam as the cylinder rises, as shown at the right in the figure. The length of the stroke is determined by stops on the rods at the sides of the pump. These rods are fastened at the upper ends to the moving cylinders. The cylinders are thus stopped before the connecting rod has reached the end of its stroke or "dead point," and therefore the sleeve continues to turn after the walking beam and cylinders have come to rest. This is made possible by the long steel springs which drive the walking beam, as they bend enough to allow the sleeve to turn a little after the walking beam has been stopped.

During this short interval, while the cylinders are at rest, the valves are reversed by means of compressed air, so that as either cylinder descends the air will flow into the exit pipe. As seen in the figure, there are two pipes running under each pump. These pipes extend up inside the pump to the top of the stationary cylinders, the ends just reaching through the bottom of the pump proper. The valve is so arranged that when one of these pipes is closed the other is open. In front of the standard carrying the driving mechanism of the pump is seen a small rod which extends below the base. This is driven from the sleeve by a pair of beveled gears, and hence it also has an oscillating movement. As soon as the

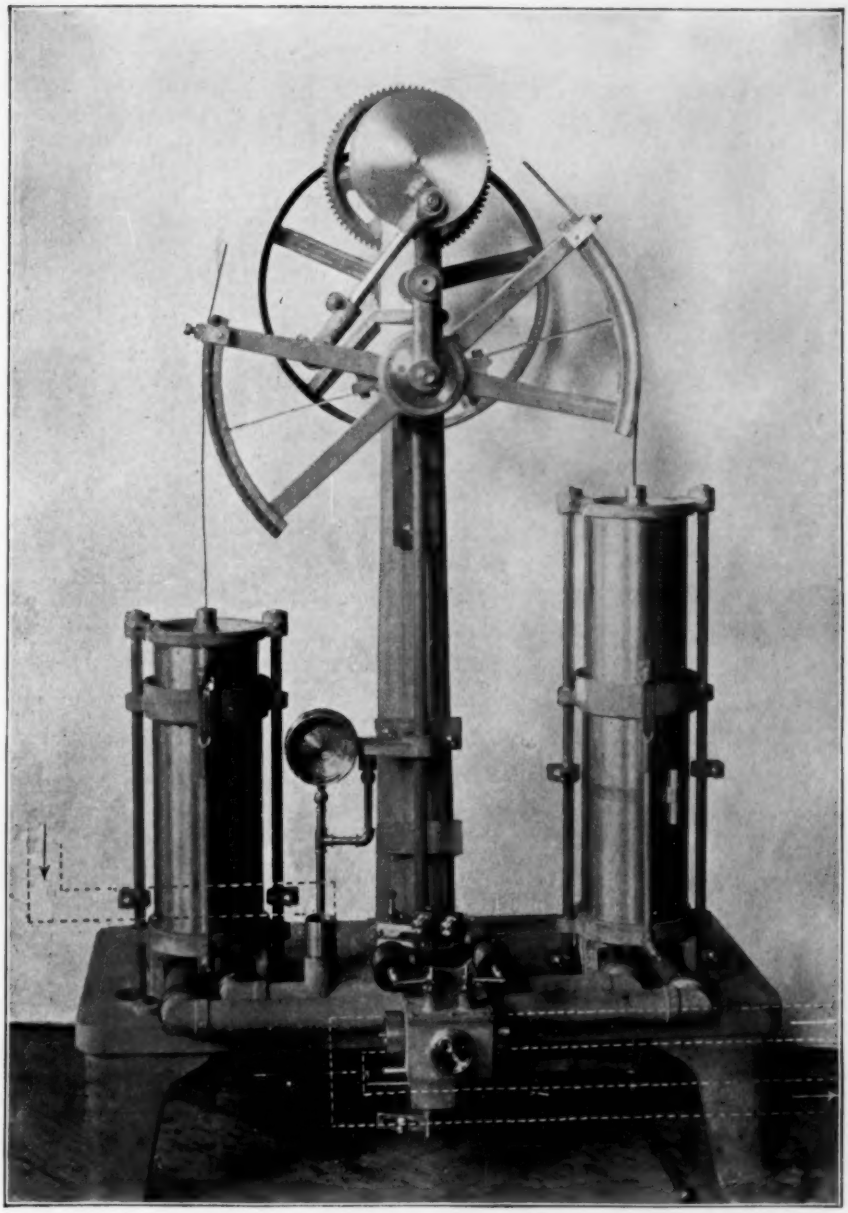


Fig. 12.

Blakeslee Meter Pump. The dotted lines show the positions of the pipes through which the main air current enters and the samples for analysis pass out.

cylinders have come to rest a port in the compressed air chamber is opened ; the air escapes into a cylinder ; the piston makes one stroke, which reverses the valves in both pumps, setting one so that air may be drawn in from the in-going pipe and the other so that the air may be expelled into the exit pipe. All this is done while the cylinders are at rest, and thus the air within them is at atmospheric pressure. The volume of each cylinder is known from its dimensions, and an automatic counter records the number of strokes.

In front of the base of the standard are seen the electro-magnets used in taking the samples for analysis. Below them is the chamber through which all of the air from the exit pipe must pass before it can escape. There are three openings from this chamber—one in front and one at either side. From the side openings are pipes (shown by the dotted lines) leading to the receptacles for holding the samples before analysis, termed briefly "pans." Likewise a pipe placed on the opening in front conducts the main current of air to the boxes surrounding the pans. This gives the same atmosphere both within and without the pans, and has been found by experiment to prevent a transfer of moisture through the sheet-rubber tops of the pans.

The method of taking the samples is as follows: Between the electro-magnets and the standard is a rachet wheel having 100 teeth. At each stroke of the pump this wheel is advanced by one tooth. Mounted on this wheel is a pin which closes an electric circuit once every revolution—that is, once every hundred strokes. The current flows through one of the electro-magnets, drawing in its plunger. This motion closes the aperture in front, at the same time opening the one at the side, and thus allowing the air from a complete double stroke (both cylinders full) to pass into the corresponding pan. The electric circuit is then broken, which releases the plunger of the magnet, and the air continues to flow through the opening in front. A second pin in the toothed wheel, on the opposite side from the first, closes a second circuit through the other electro-magnet, so that the intermediate fiftieth strokes are delivered into the other pan for duplicate analysis. This pump, although necessarily somewhat complex in construction is reliable and satisfactory in its operation.

4. *Analysis of the Samples of Air.*

The method of analysis of the air current consists in passing the sample through U tubes containing sulphuric acid for the removal of the water and soda-lime for the removal of the carbon dioxid.

These U tubes are about 12 centimeters (5 inches) in length and 1.5 centimeters (5/8 inch) in diameter. Those for the absorption of water are about two-thirds filled with pumice stone drenched with concentrated sulphuric acid. In use these tubes are laid nearly flat, with just enough incline to the tube to avoid all danger of the acid coming in contact with the rubber stoppers through which the small connecting glass tubes pass. Detailed experiments have shown that the absorption of water vapor from an air current flowing at a rate as high as 750 cubic centimeters per minute is complete by the use of one such sulphuric-acid tube until the acid has taken up 1 gram of water, after which complete absorption from a current flowing at this rate can not be depended upon.

While only one U tube is necessary for the complete absorption of the water, a system of three U tubes is used for the complete removal of the carbon dioxid from the sample. Two of these are filled with soda-lime for the absorption of the carbon dioxid itself; the third contains sulphuric acid, which serves for the collection of the water taken up from the soda-lime by the current of perfectly dry air passing over it. As the absorption of carbon dioxid takes place the yellowish color of the soda-lime gives place to the white color of the sodium and calcium carbonates that are formed, thus making it easy to see when a fresh tube is necessary. In the analysis of the incoming air, which contains very small quantities of carbon dioxid, one soda-lime tube, followed by a sulphuric-acid tube, is found sufficient, but for the outgoing air three tubes are used, as above described. When the soda-lime in one is nearly saturated the tube is removed, the second moved forward to take its place, and a fresh tube is added in place of the second. In this way the second tube in the system is always filled with fresh soda-lime. It has been found that two soda-lime tubes will remove all of the carbon dioxid from an air current flowing at a rate as high as 750 cubic centimeters per minute.

5. *Residual Carbon Dioxid and Water Vapor in the Respiration Chamber.*

The term "residual carbon dioxid and water vapor" is applied to the total amount of these materials remaining in the chamber at any given time.

In the check experiments described beyond, in which alcohol was burned, and in the experiments with man, the quantities of carbon dioxid and water vapor in the air of the chamber were found to be subject to considerable variations. In the experiments in which alcohol was burned in the chamber these fluctuations are due to the combustion of the alcohol at different rates; in experiments with a man they are due to differences in the amount of external or internal work done, and the consequent changes in the amount of material oxidized and the carbon dioxid and water eliminated.

In order therefore to determine the exact amounts of carbon dioxid and water given off during any given time from the combustion of alcohol in a lamp or of food in the body, it is necessary to know not only the amount of these respiration products in the ventilating air current during this period, but the variation of the residual amount in the chamber. For this purpose a sample consisting of 10 or 12 liters of air is drawn from the interior of the chamber through absorption tubes and the number of milligrams of carbon dioxid and water vapor per liter ascertained. This gives the total amounts of these products in the chamber the capacity of which is about 4800 liters, at the time the sample was drawn. Residual analyses are thus made at the beginning of an experiment and at the close of each experimental period.

The residual analyses therefore give data for determining a positive or negative correction which is applied to the amount of respiratory products found in the ventilating air current in order to obtain the quantities of these products actually given off during each experimental period.

(*To be continued.*)

A METHOD FOR THE STUDY OF PHOSPHORESCENT SULPHIDES.

BY FRED. E. KESTER.

WITH such phosphorescent materials as are luminous for only a short time after illumination, Becquerel[1] used the phosphoroscope for photometric measurements. A large part of his quantitative study of phosphorescence was upon this kind of materials. To obtain measurements on substances, which continue to emit light for a number of minutes, and in some cases for several hours, after illumination, he made direct observations by adjusting the intensity of his comparison surface to equality with the transient intensity of the test substance and noting the instant at which the adjustment was made.

So far as I have been able to find, later observers, notably L. Darwin,[2] E. Wiedemann,[3] H. Becquerel[4] and C. Henry,[5] have used these two methods with slight modifications to suit special needs.

1. APPARATUS.

In order to study the luminosity of sulphides of the alkaline earths between the limits imposed, on the one hand, by the intermittent character of the observations when the phosphoroscope is used, and on the other by the difficulty of making, by direct observation, a measurement of intensity of phosphorescence very soon after an illumination, I used the following device. A vertical cylinder of the test substance was rotated about its axis and was illuminated on one side through an aperture which was placed quite close to the cylinder. Then the emitted light was examined by a spectro-

[1] La Lumière, I, p. 244.

[2] Chem. News, 42, p. 302, 1880; Phil. Mag., V-11, p. 210, 1881.

[3] Wied. Annalen, 37, p. 177, 1889; Phil. Mag., V-28, p. 149, 1889; Eder's Jahrbuch f. Photographie, 5, p. 587.

[4] Comptes Rendus, 113, pp. 618-672, 1891.

[5] Comptes Rendus, 115, pp. 505-602, 1892.

meter, the slit of which was diametrically opposite the illuminating aperture. With a constant intensity of illuminating light and a constant speed of rotation, however slow, the intensity of the emitted light, as observed in the spectrometer, would, of course, remain the same, so that there would be no difficulties in making spectrophotometric comparisons, aside from those which necessarily accompany work with very weak intensities.

It was my first intention to get the test substance into cylindrical form by filling a piece of glass tubing with it; this method would have left the phosphorescent powder in its natural form. But I was unable to find a piece of tubing which did not diffuse into the spectrometer some of the light carried around from the aperture by the internal reflections within the glass. The diffusion was caused by air bubbles and milky streaks inside the glass.

I finally decided to fix upon the convex surface of a turned brass cylinder, 27 mm. in diameter, a thin layer of the sulphide, by mixing a small quantity of it with a few drops of varnish and enough turpentine to make the mixture of the proper consistency, and then painting the convex surface with it. Varnish and turpentine were chosen for this purpose because neither of them has any tendency to reduce the sulphide to a sulphate by oxidation and because the varnish, when dry, protects the material from this oxidizing action of the moisture of the air. The fact that the powder, when so treated, was far from its natural state was a serious objection to this method.

The exciting light (from an arc lamp or from the sun) was formed into a spectrum and the cylinder with its aperture was placed in that part where the efficient wave-lengths lay. It was then necessary to measure the energy in the region of the spectrum which was used in exciting phosphorescence. The usual methods of the thermopile and bolometer, all of which necessitate the use of a delicate galvanometer, were not available because of magnetic disturbances; and a photometric method was not convenient. After a number of attempts to devise a suitable method, it was suggested to me that a Crook's radiometer be built in the form which Mr. E. F. Nichols[1] had used, in some measurements of radiations of long wave-length,

[1] PHYS. REVIEW, IV., 297, 1897.

while in Berlin. This was done, the piece being made very similar in form to his.

It may be of sufficient interest to mention here a difficulty which I encountered in the process of construction of the radiometer. In a tentative form of the apparatus a metal top, with a vertical brass tube soldered into it, was used; into the brass tube was sealed the tube of a glass stop-cock by means of ordinary sealing wax. A number of observers had had trouble with sealing wax when used in the joints of high vacuum pieces, but from all the statements noticed the trouble seemed to arise from leakage. This it was hoped to avoid by making between the glass and brass tubes (the brass being on the outside) a long, firm seal. However, in this form, the enclosure could not be maintained at a sufficiently low pressure, and a search for leaks was commenced. After some time it was noticed that the pressure did not rise steadily, but came up to a certain value and then hung there, indicating the presence of a vapor tension rather than of a leak. The sealing wax was suspected at once and in order to try it a few small pieces were placed in a clean vacuum tube which was then pumped to a high vacuum and sealed off. The pressure in the tube (indicated by the character of electric discharge through it) rose to one or two tenths of a millimeter in about half an hour and then remained constant.

A glass top was then ground to fit the metal body of the radiometer, and the tube of the glass stop-cock welded to it. Even in this final form the piece leaked a little, so that it was necessary to standardize it from day to day by means of a constant source of radiation. A Hefner photometric lamp was used for this purpose.

The arrangement of pieces was, then, as shown in Fig. 1. The aperture A in the wall of the dark room was illuminated from without by an arc lamp, with suitable condensing lens, or by sunlight, and the spectrum of the light brought to a focus with the blue end on the cylinder T. The mirror M had its upper edge on the same level with the lower edge of the aperture A, and was so placed as to reflect light, into the radiometer, of the same wave-length as that used in exciting phosphorescence, the spectrum being so adjusted as to cover both M and A.

The standard for photometric comparisons was a magnesium

oxide surface illuminated by an acetylene flame which was furnished with gas at constant pressure. The light diffused from the surface reached the spectrometer through two Nicol prisms, P and A, and

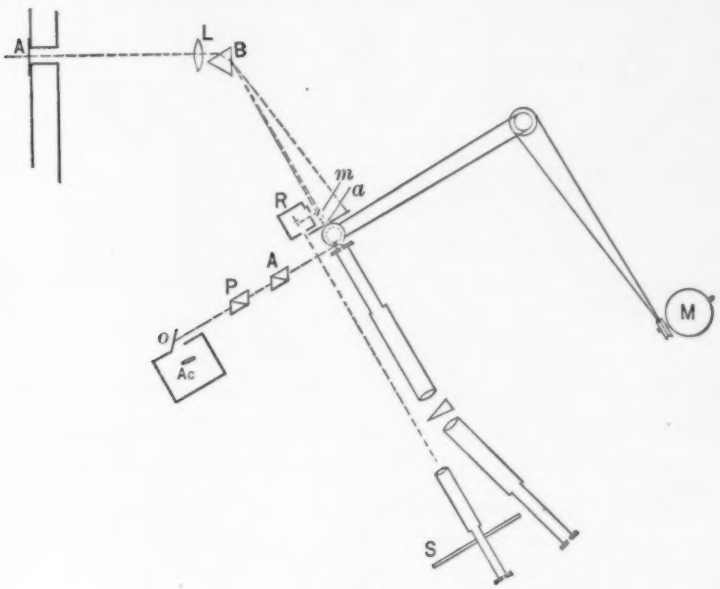


Fig. 1.

a total reflection prism which covered the lower half of the collimator slit. The upper half of this slit received light from the phosphorescent cylinder.

Finally, the spectra of the phosphorescent light and of the diffused light from the magnesium oxide surface were formed, one above the other in the field of the eye-piece of spectrometer, by a low dispersion prism of crown glass with a 30° angle. It was necessary to use such small dispersion as this prism gave because of the feebleness of phosphorescent light. The eye-piece contained the usual narrow aperture for cutting out of view all parts of the spectra except those which it was desired to compare. Then when the chosen parts of the spectra were made of the same intensity by adjusting one of the Nicol prisms, the intensity of phosphorescence at this wave-length was measured by $\sin^2\theta$, where θ is the angle between this position of the Nicols and the crossed position.

The cylinder T was rotated at a constant speed by a small motor M driven by current from storage cells. By the use of a system of pulleys the speed could be varied from about 0.03 sec. to 7 or 8 sec. per revolution.

As soon as readings were commenced it was found that the arc lamp as a source of exciting light would have to be discarded; its fluctuations were much too rapid to be followed by the luminosity of the sulphide. Observations could be taken only with sunlight on clear days.

On account of the late date at which the necessary apparatus was completed and, too, because of the scarcity of clear sunshine, I have been unable to make observations on more than one material—calcium sulphide.

2. OBSERVATIONS.

To afford a means of correcting for uncontrollable variations in the intensity of the exciting light it was necessary to establish, first of all, a relation between the intensity of phosphorescence and the

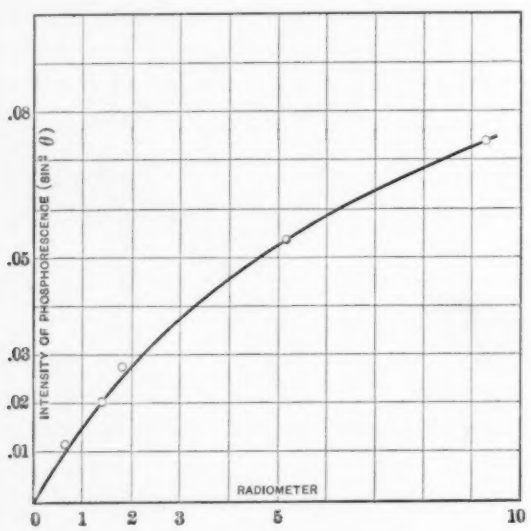


Fig 2.

intensity of illumination. The intensity of the exciting light was varied by interposing pieces of blue glass in the path of the ray of sunlight and was measured by the deflections of the radiometer, Mr.

Nichols having found that, under proper conditions, the deflections were proportional to the energy of radiations.

In obtaining these preliminary readings, the carbon bisulphide prism, which was used in order to obtain sufficient separation of the

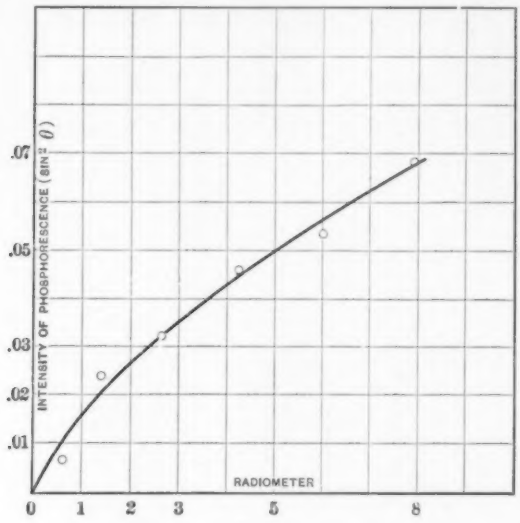


Fig 3.

wave-lengths of sunlight within the necessarily short distance *BT*, gave some trouble. The action of the light in traversing the prism decomposed the bisulphide, setting free small particles of sulphur which diffused light in all directions. Some of this stray light, traveling in the direction of *m* and *a* caused an increase in the deflection of the radiometer but no corresponding increase in the luminosity of the phosphorescent material. A couple of curves obtained with bad charges of bisulphide are shown in Figs. 2 and 3.

Each point is obtained from averages of from three to five readings of the radiometer and of the Nicol prisms. To obtain the intensity of phosphorescence from the Nicol prism readings it is sufficiently accurate to take the square of the sine of the average angle.

A set of readings taken with a fresh charge of bisulphide is given in the table following; it shows to what degree of accuracy the settings of the Nicols were made. The errors in this column of readings made it desirable to have a larger number of observations in each group, but time did not permit.

Radiometer.			Nicol Prisms.		
Readings.	Zero.	Deflection.	θ	Av. θ.	$\sin^2$ (Av. θ.)
11.4 11.3 11.4	3.9	7.47	18.0 16.0 16.8	16.9	.0853
10.8 10.7 10.7 10. 8	4.0	6.75	16.8 15.4 16.2 15.8	16.05	.0765
9.1 9.2 9.1	4.0	5.13	13.0 12.8 12.8	12.87	.0500
7.4 7.2 7.2	4.0	3.27	11.8 12.2 11.8	11.93	.0432
6.9 6.9 6.9	4.0	2.90	10.2 9.8 10.2	10.07	.0315
6.2 6.1 6.3 6.2	4.0	2.20	8.2 9.0 7.8 8.0	8.25	.0210
5.1 5.1 5.1	4.0	1.10	6.2 7.4 6.8	6.80	.0140

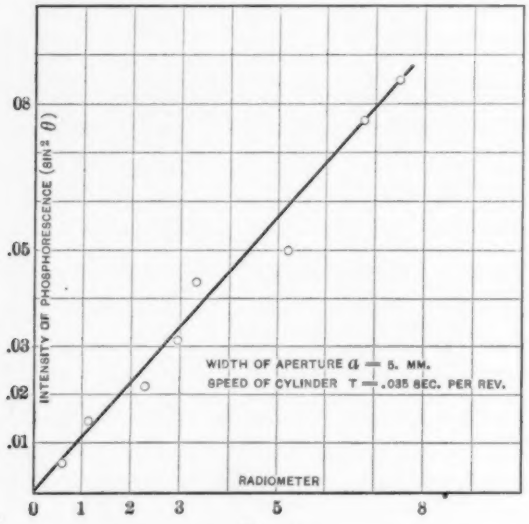


Fig 4.

The curve of Fig. 4 is plotted from this set of readings and indicates that the luminosity of the sulphide is proportional to the

intensity of illumination, under the conditions of the present apparatus. Fig. 5 gives another curve of the same type, taken with a different width of aperture a and slightly different position of the spectrum of sun light. For all wave-lengths of exciting light, widths

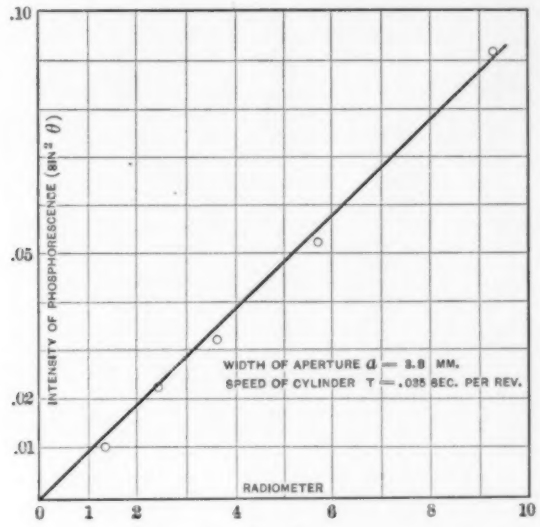


Fig 5.

of aperture a, and speeds of rotation which were tried it was found that the curves of intensities were straight lines.

Then keeping the intensity of illumination constant, or correcting, by means of the above curves, for the uncontrolable variations, and keeping the speed of rotation constant, the effect of varying the width of a was determined. During these observations the intensity of the exciting light would, of course, vary somewhat. The variation was corrected for by dividing $\sin^2\theta$ by the radiometer deflection, which operation is directed by the proportionality existing between the intensities. Fig. 6 is a curve showing the relation between the luminosity and width of aperture.

The relation between intensity of phosphorescence and speed of rotation of the cylinder is shown by Fig. 7. Here each point is obtained from an average of from eight to ten observations.

With the width of aperture A, which it was necessary to use, the spectrum of the sunlight was so impure that most of the wave-

lengths, which were efficient in producing phosphorescence, were to be found in the aperture *a*. On account of this it was found impossible to obtain accurately by measurements the relation between the luminosity and the wave-length of exciting light. For this purpose a flat surface was painted with the sulphide of calcium and ex-

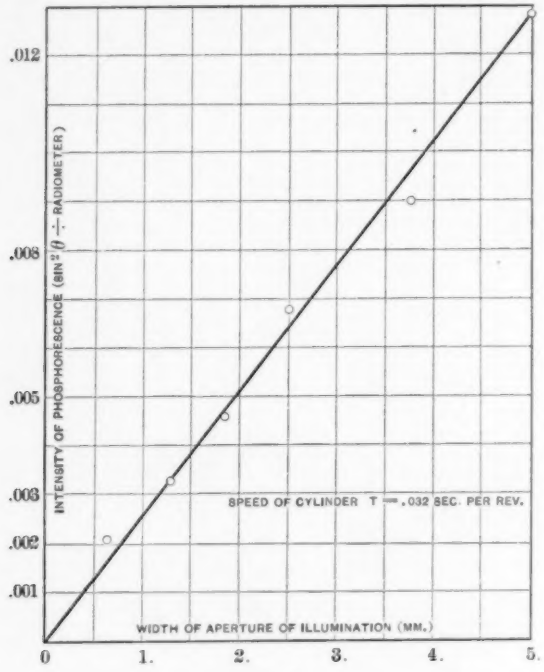


Fig 6.

posed in the spectrum from a narrow aperture. By noticing the luminosity soon after illumination a visibility curve was sketched showing approximately the desired relation.

And in the case of constant conditions of the cylinder *T*—as to illumination and speed—it was useless to compare the intensities at various regions of the spectra of the emitted light and of the light from the surface *o* because of the uneven distribution of energy in the spectrum of the acetylene flame. A visibility curve of intensity and wave-length of phosphorescent light was made.

These last two curves are drawn in the same figure (Fig. 8) in order to show more clearly the relation between the wave-lengths

of exciting and emitted light. The ordinates of the lower curve represent the intensity of the whole group of wave-lengths of the

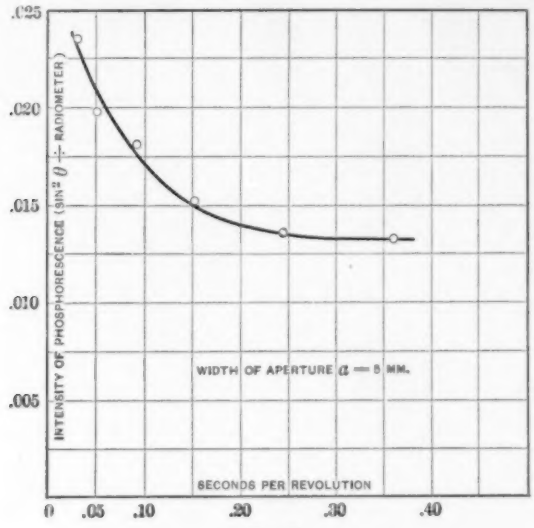


Fig 7.

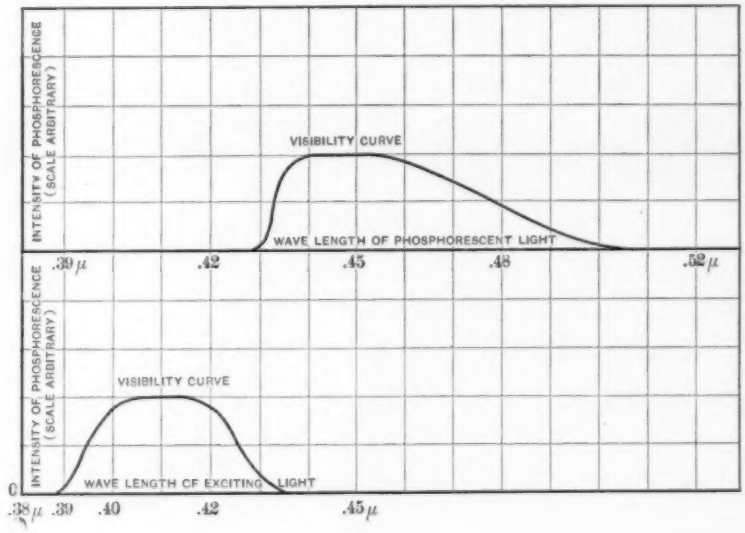


Fig. 8.

phosphorescent light. With a wider dispersion of the illuminating light, giving greater purity of spectrum than the present arrange-

ment of apparatus affords, and thereby permitting of measurements on the wave-lengths of exciting light, it will be possible to separate this curve into its component curves and, by so doing, show quite definitely the relation between the wave-lengths of exciting and of emitted light. This relation would be of special interest in those sulphides which have more than one band in their spectra.

It may be shown by a discussion of the curve of intensity of phosphorescence and time of revolution of the cylinder, in connection with the curves of phosphorescence and width of aperture, that there are no definite curves of increase and decrease of luminosity during and after illumination; in other words, the rate of increase or of decrease at any intensity of phosphorescence depends upon the previous treatment which the luminous material has undergone. This is a fact which E. Wiedemann[1] had noticed in the case of Balmain's luminous paint and which he stated to be true of the sulphides of the alkaline earths, either from a knowledge of the constituents of the paint or from independent observations made on these sulphides.

The peculiarity may be shown by means of the present curves as follows: Assume that there are definite curves such as shown in

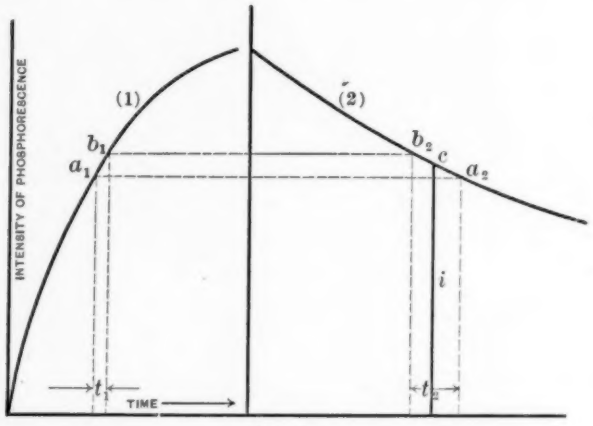


Fig. 9.

Fig. 9, curve (1) being for increase and (2) for decrease of luminosity. Then when the cylinder of material has reached a steady

[1] Weid. Annalen, 37, 177; 1889; Phil. Mag., 15-28, 149, 1889.

condition for a certain speed of rotation and a certain intensity of illumination, the material is going through some such cycle as a_1 b_1 b_2 a_2 for each revolution of the cylinder. Observation by the spectrometer is made as the material passes the slit, namely, at the condition represented on the curve (2) by the point c. Now since the increase in intensity from a_1 to b_1 is equal to the decrease from b_2 to a_2, the ratio of the slopes of the two curves at this intensity is equal to the inverse ratio of the times of illumination and insulation. But we can work at the same intensity of phosphorescence by decreasing the width of the aperture a and increasing the speed of rotation; in so doing we have changed the above ratio of times and consequently have no determined slope for the curves at the intensity considered.

So far, therefore, as the present observations are concerned the behavior of the calcium sulphide will have to be defined in terms of the apparatus used. There seems to be no way of so combining the results as to show the behavior in a more absolute manner. For this reason it is unnecessary to give the various times of illumination and of insulation in more detail than is done in the preceding pages and accompanying figures.

DEPT. of PHYSICS, CORNELL UNIV., June, 1899.

THE PHOTOMETRIC STUDY OF MIXTURES OF ACETYLENE AND HYDROGEN BURNED IN AIR.

BY LEON W. HARTMAN.

THE steady advance of acetylene as an illuminant justifies any investigation of the light and color properties of the acetylene flame burned under varying conditions. This investigation will be devoted primarily to studying the photometry and the spectrophotometry of the flame produced by burning in air varying mixtures of acetylene and hydrogen.

Very little reliable information concerning the cost and efficiency of acetylene as an illuminant has been given in recent years. Violle[1] found that an acetylene burner giving 100 candle power under a pressure of 30 cm. water, was twenty times more efficient than a coal gas burner of the Bengel type giving one carcel, or 9.6 candles per 105 liters; and at least six times more efficient than the same coal gas, burned in an Auer burner, giving one carcel per 30 liters of gas burned. Although in 1896 acetylene cost in Paris five times as much per cubic meter as ordinary illuminating gas, yet it was more economic as an illuminant since it gives fifteen times more light for an equal volume.[2] Hospitalier[3] made a comparison of the cost per carcel hour between a number of illuminants, from which he concludes that acetylene is about one-third as expensive as the incandescent lamp and about one-fourth as costly as ordinary gas burning in the butterfly tip. In this connection the results obtained by Wedding are interesting.[4] He studied the effect upon candle power of adding acetylene in varying proportions to ordinary illuminating gas. He found, for example, that without acetylene the burner consumed fifteen liters per bougie hour, and that with twelve parts of acetylene per hundred the burner burned four liters per bougie

[1] L'Éclairage Électrique, VI., p. 319, 1896.
[2] L'Éclairage Électrique, VI., pp. 133-4, 1896. [3] Do.
[4] L'Éclairage Électrique, VI., p. 88, 1896.

hour. His results are indicated in Fig. 1, where specific consumption, or the amount consumed per hour, is plotted as ordinates and the percentage of acetylene as abscissæ.

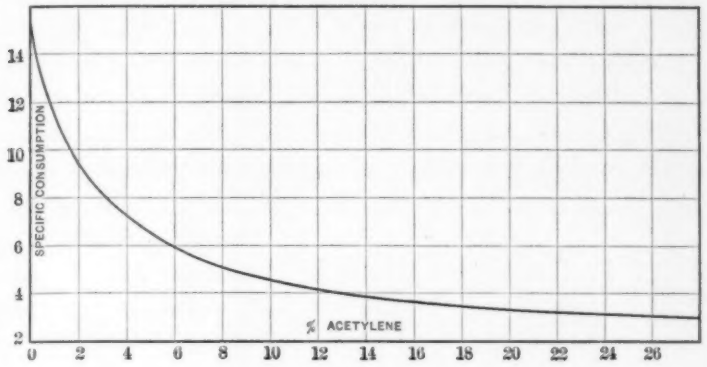


Fig. 1.

Wedding's curve, showing relation between specific consumption and percentage of acetylene in illuminating gas.

It has been found that the gas as it is given off from the acetylene generator contains impurities. In a number of the continental cities of Europe where this gas is used on a large scale as an illuminant, the removal of these impurities was a serious problem. It is well known that the peculiar pungent odor of common acetylene is due to the presence of phosphoretted hydrogen. To remove this, Lunge and Cedercreuze suggest the use of calcium hypochlorite.[1] More serious still are two other impurities found in ordinary acetylene, viz., arsine and hydrogen sulfide. In a series of analyses of common acetylene Giraud found[2] in a cubic meter of gas these impurities in sufficient quantities to warrant considerable prudence in the use of the gas.

Several methods of purifying the gas have been suggested. The following simple method of removing these impurities has been used by Berge and Reycher.[3] The gas from the generator was first passed through a solution of caustic potash. This removed the hydrogen sulfide by the precipitation of potassium sulfide. The gas

[1] Electrician, XLI., p. 517.
[2] L'Éclairage Électrique, VIII., p. 319, 1896.
[3] Bulletin de la Société Chemique de Paris, XVIII., p. 218, 1897.

was then passed through two Wolff bottles in series each containing a solution of mercuric chloride, which had been slightly acidified by adding dilute hydrochloric acid. Probably the resulting products were the phosphide and the arsenide of mercury, in which there was doubtless some crystalline mercuric chloride. After passing the gas through these solutions Giraud found it free from these obnoxious impurities. Their method was followed in this investigation whenever purified acetylene was used.

Turning to the photometry and the spectrophotometry of acetylene, one is confronted by the fact that there is an exceedingly small amount of published matter on this phase of the subject. Violle[1] mentions some photometric and spectrophotometric work which he did with acetylene. The results of his photometry have already been given.[2] As a result of his other work he says: "The spectrophotometer shows besides that in all the extent of the spectrum from *C* to *F* that the light of acetylene differs little from that of fused platinum." He describes the burner used and the diaphragm in front of the flame; this part of his apparatus was almost identically the same as the secondary standard used in this investigation. This standard will be described later. Fery, "On the photometry

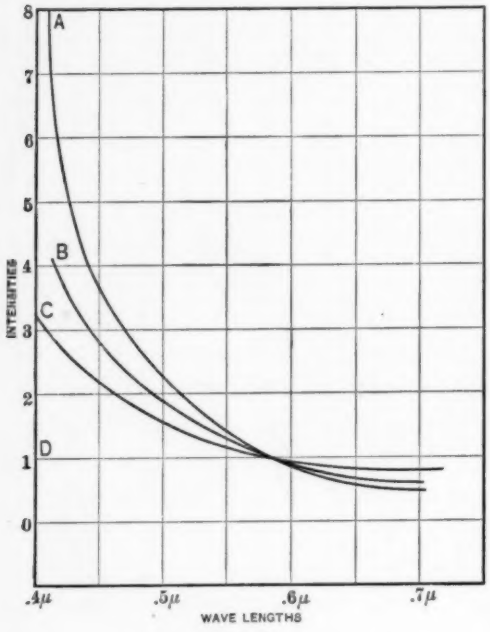


Fig. 2.

Spectrophotometric curves by Sharp. A—Acetylene in oxygen. B—Acetylene, 50%, and hydrogen, 50%, in oxygen. C—Acetylene in air. D—Kerosene lamp.

[1] C. R., CXXII., p. 79–80; L'Éclairage Électrique, VI., p. 178, 1896.
[2] Vide, p. 1.

of acetylene,"[1] used the Carcel lamp as a standard; also the Drummond and magnesium lamps. He likewise gives neither data nor curves.

The Physical Department placed at my disposal a lantern slide on which were spectrophotometric curves[2] of acetylene burning in oxygen, acetylene fifty per cent. and hydrogen fifty per cent. burning in oxygen, acetylene burning in air, all of which sources were compared with the kerosene lamp as a standard. Inasmuch as these curves are very closely related to the subject under consideration, they have been incorporated in this résumé and are given in Fig. 2.

Apparatus and Methods.

The acetylene used in this investigation was generated in a generator designed by Dr. Sharp of the Physical Department and made expressly for the work in this laboratory. The gas was stored in tanks over water saturated with acetylene.

The mixtures of acetylene and hydrogen were likewise stored in tanks over water saturated with acetylene. At first thought, this might appear to be an unsatisfactory method since the percentage composition would be very apt to change, either by the water in the tank absorbing or giving off acetylene. Professor Lewes[3] found, in a similar mixture stored over water, that the proportion of acetylene present in the gas, as determined by analysis at the burner, was not the same as in the gas within the holder, although the water in both meter and holder was saturated as far as possible with the gas. Yet, as his analyses show, the precaution of analyses at the burner was an important one. Accordingly in each case as the gas came off from the tank, after having been thoroughly mixed, two or more analyses of the mixture were made at the burner. In analyses made at the beginning and at the end of a set of observations, in which time two or three hours might elapse, no noticeable change was observed. If an interval of several days intervened between two analyses of a given mixture, a change of two or three per cent. might occur.

[1] L'Éclairage Électrique, VIII., p. 54, 1896.

[2] These curves were plotted by Dr. C. H. Sharp from data that he had taken in this laboratory.

[3] Chemical News, LXXI., p. 190, 1895.

The method of analysis was as follows: It was known that an ammoniacal solution of cuprous chloride would absorb acetylene, forming copper acetylide, while the hydrogen would not be affected. Hence measuring out 100 c.c. of the mixture in a Hempel burette and then passing the gas into a compound Hempel pipette for solids and liquids containing such an ammoniacal cuprous chloride solution, the acetylene would be wholly absorbed. Upon passing the remainder of the gas back into the burette the percentage of acetylene could be read directly. The preparation of the ammoniacal cuprous chloride solution was according to Sandmeyer's method.[1]

Throughout this work two general types of burner have been used. One form of burner was made by drilling a very small hole through a tightly fitting brass plug, which replaced the lava tip in an ordinary gas burner. The second type was the Nephey burner. Three forms of this were used; a single, a double and a triple burner. Figs. 3 and 4 will help to explain this form of burner. The essential feature is the lava tip, of which Fig. 3 is an enlarged lateral section and Fig. 4 is a trans-section. The outlet of the tip is a minute passage through the lava, ending in a chamber at the apex of a flat cone. Several passages, *a*, at regular intervals extend from this chamber to the atmosphere outside, thus allowing the gas to mix with air before it escapes through the larger bore, *b*, at the end of the tip. The single tip gives an elongated cylindrical flame ending in a tip very similar in shape to that of the Bunsen burner. In the triple burner, the three tips are arranged as in Fig. 5. Each flame impinges upon the others at an angle, thus producing a broad fan-shaped flame, whose plane is at right angles tothe plane containing the three tips. In the double burner the central tip of the triple burner is wanting. The purpose of this type of burner is, obviously, to secure complete combustion; it was therefore used when the percentage of acetylene was high.

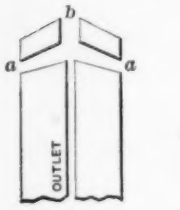


Fig. 3.
Lateral Section of Lava Tip.

Fig. 4.
Trans-section of Lava Tip.

[1] Berichte der Deutschen Chemischen Gesellschaft, XVII., p. 1633 b.

As a primary color standard in the spectrophotometric work, the Hefner lamp was used. As a primary standard in the photometric work, a standard incandescent lamp was used. As a secondary standard, however, the triple Nephey burner was found to be very satisfactory. It was observed that the central portion of the flame appeared uniform throughout a considerable range of pressure. Touse this limited portion of the flame, an half-inch diaphragm was fastened on the burner so that the diaphragm was in front of this uniform area. Thus, the triple Nephey burner under a given pressure was used as a secondary standard in the spectrophotometric work.

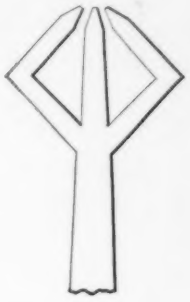


Fig. 5.
The Triple Burner.

To obtain the various measurements of gas pressure, a pair of burettes graduated in tenth centimeters and bent into **U**-tubes, were filled with colored water and used. By means of a glass **Y** in the tube leading to the burner, the pressure on the burner could be measured. To prevent rapid evaporation of the water the free end of the **U**-tube contained a cork having a small groove cut along its sides. Whenever measurements involving volume of gas were required, a standard Elster gas meter was used.

For the photometric work a track divided into one thousand divisions was used. Upon this track the photometer could be moved back and forth until equal intensities were secured, and the reading was then taken. The lamp at one end of the bar being a standard 16 candle-power incandescent lamp, the intensity of the unknown source could be readily computed. Two photometers were used: a Lummer-Brodhun and a Bunsen disk photometer. The former was preferable in cases where the color of the two sources was alike, and in cases where the intensities were weak. The disk photometer gave better service when the intensities were strong, and when the color of the two sources was unlike.

The stationary horizontal slit spectrophotometer used in this investigation was devised by Professor Nichols and is fully described elsewhere.[1]

[1] PHYSICAL REVIEW, Vol. II., No. 8; Nichols' Laboratory Manual, Vol. II., p. 360.

The first results of photometry with the secondary standard were very unsatisfactory. The candle-power for given pressure varied more or less from day to day. To remedy this error a gas cushion was introduced in the tube leading from the Y to the burner. This gas cushion was made by soldering into the ends of a liter tin can two pieces of metal tubing, over which the rubber tubing of the burner fitted tightly. At the orifice of the can nearer the burner was a minute diaphragm. The result of this change was to produce a more constant flow of gas and to give a uniform candle-power under a given pressure. It is needless to say that at each observation the primary standard (*i. e.*, the standard 16 candle-power incandescent lamp) was adjusted at 16 candle-power by bringing its voltage to the proper value, and the unknown source was always carefully adjusted in position.

In the first series of spectrophotometric measurements, considerable difficulty was experienced in getting the two fields of the telescope exactly uniform in intensity. Although the field is very narrow and therefore free from a mixture of different wave-lengths, yet its great extent from right to left made it extremely difficult to decide when the two fields were equally bright. For example, if the eye could be held in a position where the line of sight to the narrow dark division between the two fields was coincident with the principal axis of the lens system of the telescope, there would be no difficulty; but if, when the intensities of the two fields were the same, the head were moved slightly to the right, the left field would appear the brighter; and *vice versa*. To overcome this a thick wooden cap was fitted over the eyepiece of the telescope and through the center of this cap a hole about ½ millimeter in diameter was bored. This cut down the length of the field within narrow limits. To see the line of division between the two fields after this change, the line of sight had to approximately coincide with the principal axis of the lens system of the telescope.

To avoid any instrumental error in the spectrophotometric work, the standard source and the unknown source were frequently interchanged. Accordingly, two sets of data were often obtained for a given mixture. The curves showed no marked change in form as a result.

Curves and Results.

The calibration of apparatus was naturally the first work to be performed. The spectrophotometer was calibrated by identifying the principal Fraunhofer lines of the solar spectrum, whose wave-lengths were known, and noting the position of the telescope on the graduated scale along which it moves. Plotting wave-lengths for abscissæ and scale readings for ordinates a straight line resulted. The Vierordt slits of the spectrophotometer collimator were also calibrated by measuring under a microscope the width of the slits for a given turn of the screw.

It was found desirable to know the rate of flow of gas with change of pressure. To determine this, the single tipped Nephey burner was calibrated by allowing the gas to flow through a standard Elster gas meter in series with the burner. Thus, choosing certain pressures and keeping them constant for five or ten minutes, and then noting the exact volume of gas that passed in the given time, one had sufficient data for a curve. Plotting liters per minute as ordinates and pressures in centimeters as abscissæ, the resulting curve was approximately a parabola. Calibrating the half-foot Nephey burner likewise, another parabola was obtained. In these measurements the pressures were carried up until the flames began to hiss violently. As soon as hissing begins the parabolic form of curve does not appear to continue.

In this connection it will be interesting to note the results that were obtained by burning purified acetylene, under varying pressures, as a standard of light. The burner used was the triple Nephey burner with the diaphragm. As a result of a series of measurements, taken under varying atmospheric conditions, the curve in Fig. 6 was drawn. With but few exceptions the variation of the measurements from this curve was less than one per cent. These reults suggest the possibility of using purified acetylene, burning under the conditions described, as a standard source of candle-power. This phase of the subject is worthy of a more thorough investigation than time permitted here. The method of purifying the gas has already been described.

Reference has been made to the difficulty encountered in making the spectrophotometric measurements and to the method adopted in

overcoming it. But still there was a possibility of a considerable range in making the settings of the slit. To lessen the probability of error in these measurements, the following criterion was adopted. The slits on the side of the unknown source were opened to a given

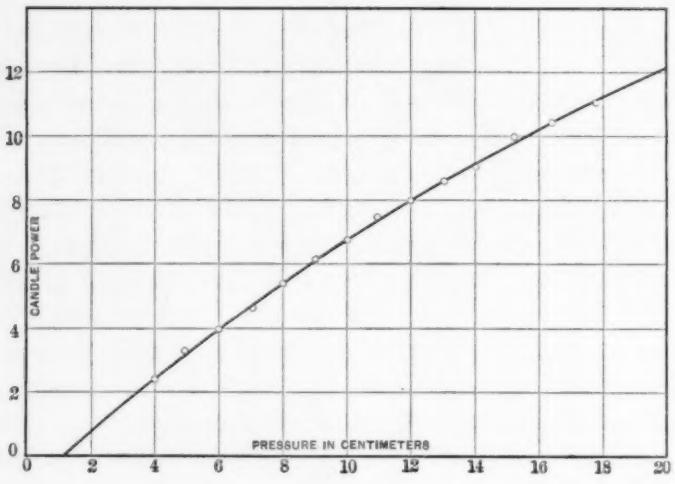


Fig. 6.

Candle-power. Pressure curve with purified acetylene.

position for the set of observations in question. Three settings of the other slits were then made, in which great care was exercised to get the two fields of the telescope exactly the same in intensity, and then the mean of these three readings was taken. In turn several settings of these slits (*i. e.*, the slits on the side of the secondary standard) were taken, until eight readings were obtained, no one of which varied from the mean of the first three readings by more than six or eight divisions. The mean of these eight readings was then taken as the width of the slits on the side of the secondary standard. The drum on the side of the unknown source was generally set at 50 or 100 divisions.

It is obvious that if I_s denote the intensity of the secondary standard and I_x the intensity of the unknown source, and if W_s denote the width of slit set for the standard and W_x the width for the unknown source, the following relation is true

$$I_s : I_x :: W_x : W_s .$$

Therefore

$$I_x = \frac{I_s W_s}{W_x} .$$

If we consider I_s unity, the intensity of the unknown source may be taken as the ratio of the slit widths. Plotting wave-lengths as abscissæ and intensities, or ratio of slit widths as ordinates, a set of curves was obtained. Finally, the value of the ordinate corresponding to the D line was taken from each curve and called unity. Each point upon the given curve is then reduced to the same scale by using the value of the ordinate corresponding to the wave-length 0.589 μ as a dividing factor. Plotting these new ratios as intensities and wave-lengths as abscissæ, another set of curves was obtained, a few of which are given in Fig. 7.

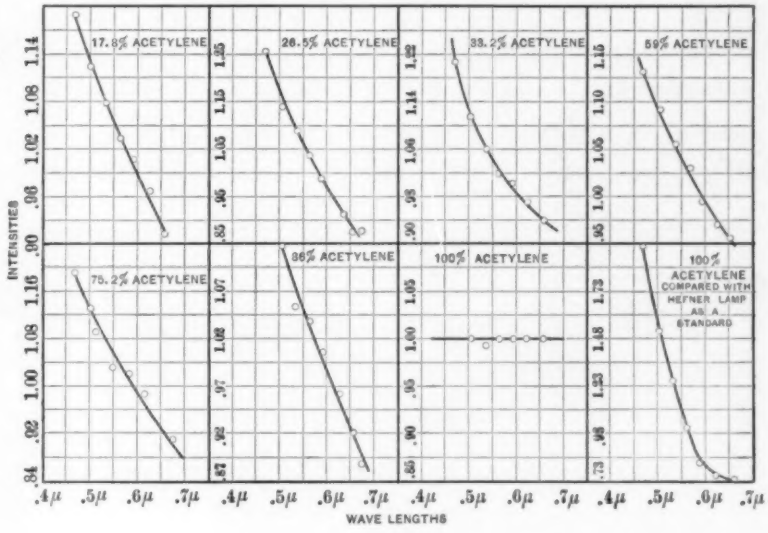


Fig. 7.

Hydrogen-acetylene spectrophotometris curves.

From a study of these curves it will be seen that the acetylene-hydrogen flame is richer in the short wave-lengths than the flame of the secondary standard burning common acetylene. Moreover, the color properties of the flame appear to be independent of the amount of hydrogen in the mixture. Upon going to the limit this statement would not hold true.

It may be well to note that in these curves, by percentage of acetylene is meant the percentage of acetylene by volume as determined by two or three analyses of the given mixture. These

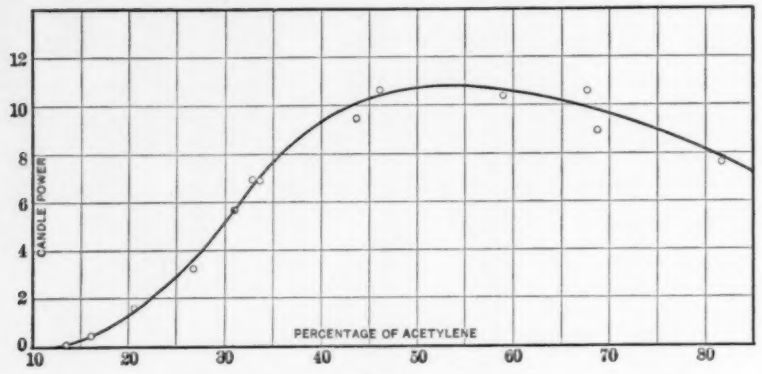


Fig. 8.

Variation of candle-power of the brass tip with change of percentage of acetylene in the mixture.

analyses were usually made within an hour of each other and the mean was then taken. If the percentage of acetylene in the mixture

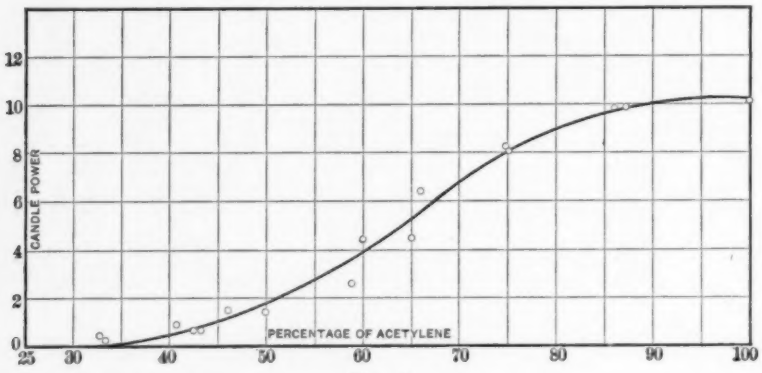


Fig. 9.

Variation of candle-power of the small lava tip with change of percentage of acetylene in the mixture.

was above forty per cent., the lava tip was generally used at a gas pressure of ten centimeters; if the percentage of acetylene was below forty per cent., the brass tip was used at a gas pressure of four centi-

meters. The brass tip was used, however, to obtain candle power throughout a wide range of percentages.

If the percentage of acetylene in the various mixtures be plotted as abscissæ and the candle-power of the brass tip be taken as ordinates of one curve and the candle-power of the lava tip be taken as ordinates of another curve, the curves in Fig. 8 and Fig. 9 are obtained. In the case of the brass tip, it will be seen that the candle-power reaches a maximum and then falls away with increasing percentage of acetylene. This is due to the incomplete combustion of the gas after a given percentage of acetylene in the mixture has been reached. In case of the lava tip, the flame, with low percentages of acetylene, appears much like the flame of burning hydrogen; at first, it slowly increases in candle power with increasing percentage of acetylene, and does not reach the stage of incomplete combustion as is shown by the curve.

In conclusion, I desire to call attention to the difficulty that was experienced, in the first series of observations, in determining the

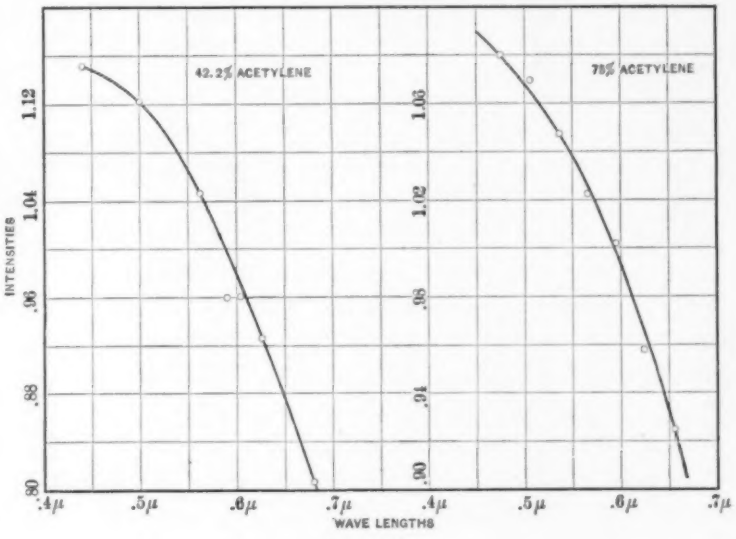


Fig. 10.

curvature of the curves obtained from the spectrophotometric measurements. For example, one would hesitate before saying that the two curves in Fig. 10 are incorrect, yet their curvature is directly

opposite to that in the curves of Fig. 7. The results of my first measurements, giving the uniform curve on the left side of Fig. 10, prejudiced me for a time in favor of that form of curve. The majority of my curves, however, had a downward inflection. This led me to plot all of the curves of doubtful curvature with as much of a downward inflection as I could consistently give them. I am inclined to believe, however, that the amount of curvature has but little significance. These two curves are the only ones that have been rejected because of their curvature and they are introduced here to show what apparently consistent curves it is possible to get in similar measurements.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY, June 30, 1899.

A PHOTOGRAPHIC STUDY OF ELECTROLYTIC CELLS.

By Rolla R. Ramsey.

WHILE making preliminary experiments with a view of using Töpler's "Schlierenapparat"[1] as a possible means for the study of vibrating films as suggested by Dr. A. G. Webster, the idea occurred to me of using the apparatus to study electrolytic action. The apparatus, as shown in diagram, is arranged as follows: S_1 is an illuminated adjustable slit, the image of which, by means of the lens, L_1, is thrown on a second adjustable slit, S_2. An electrolytic

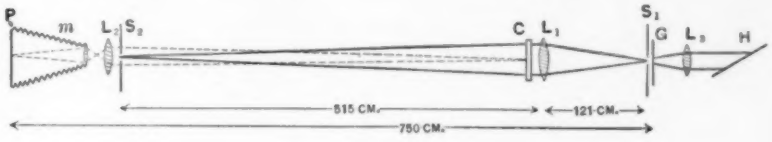


Fig. 1.

cell, C, is placed between L_1 and S_2 near to L_1. The image of C is projected on the plate in the camera at P by means of two lenses L_2 and M. L_1 is an achromatic lens of 5 cm. diameter and 93 cm. focal length. L_2 is a photographic lens of 25.5 cm. focal length. M is a 3 cm. focal length microscope objective. S_1 is illuminated with sunlight by means of a cylindrical lens L_3 and a heliostat H.

The principle of the "Schlieren-methode" is, that if the medium between S_1 and S_2 is homogeneous, then the image of S_1 will be brought to a sharp focus at S_2, which has been placed at the conjugate focus of S_1. If the slit of S_2 is made to coincide with the image of S_1, then the illumination on the screen P will be uniform. Moving the slit S_2 up will intercept the light and the screen will suddenly become dark. If the medium between S_1 and S_2 is not homogeneous, then the image of S_1 will not be sharp and moving S_2 up will intercept the light from certain portions of the field, causing it to be blotched or spotted, "Schlieren." Intercepting the lower part of the image will cause certain portions to be light, while intercepting the upper will illuminate what was dark in the first case and darken the former bright portions. The homogeneity of

[1] Pogg. Ann., 131, 33 and 180, 1867.

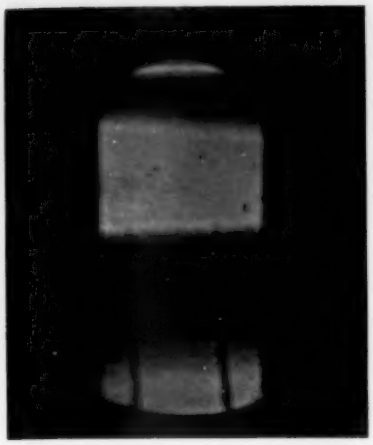
medium will be violated by heating the air, by inserting a cell in which liquids of different densities are placed, or by an electrolytic cell having a current flowing through it. The cell C is made of two pieces of plane optical glass, the inside dimensions of which are, width 2.2 cm., thickness .4 cm. The electrodes are made of strips of commercial sheet zinc. The electrolyte is a 10% solution of sinc sulphate (10 gm. $ZnSO_4$ in 90 cu. cm. of water). The solution is a clear liquid, which, when placed in the cell, has every appearance of water to the naked eye.

The accompanying photographs will illustrate the results. No. 2 shows the current passing up through the electrolyte. Since the anode is being dissolved and the cathode plated, we have changes of density at the two electrodes. A dense solution, which is seen to be falling, is formed at the anode. A corresponding light solution, which rises to the surface, is formed at the cathode. The portion between the two electrodes is uniform and, therefore, the appearance is dark. The light in this case is taken from the upper part of the slit. In No. 4 we have the same cell except that the current is reversed, that is, passing down through the solution. The dense solution is falling from the anode and the rare is rising, making a variable density between the two electrodes. Light is taken from the upper part of slit the same as in No. 2. No. 15 shows vertical electrodes. The current causes a stream of dense solution to flow from the anode. No. 15 also shows a characteristic stratification of the solution between the two electrodes. A horizontal layer of dense liquid is invariably formed at the lower extremities of the electrodes. Light is taken from the center of the slit. No. 11 is taken from a 5 cm. cubical cell made of plate glass with horizontal plate electrodes. The current is passing down through the liquid. The light is taken from the upper part of the slit. Nos. 32 and 33 illustrate the difference in the effect by taking light from the upper or lower portions of the slit. No. 32 was taken from the lower part of the slit, while No. 33 was taken from the upper. They were taken one after the other as quickly as possible, the only change being that of moving S_2 up a short distance. It will be noticed that one is the exact negative of the other.

The time of exposure varied from one to four seconds, although plates were taken with an ordinary instantaneous shutter.

CLARK UNIVERSITY, JUNE 14, 1899.

No. 2



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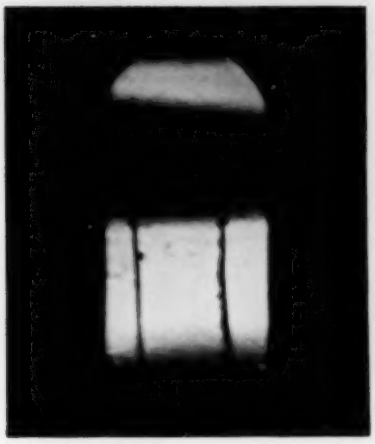

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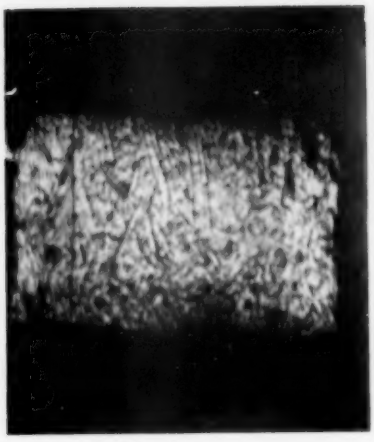

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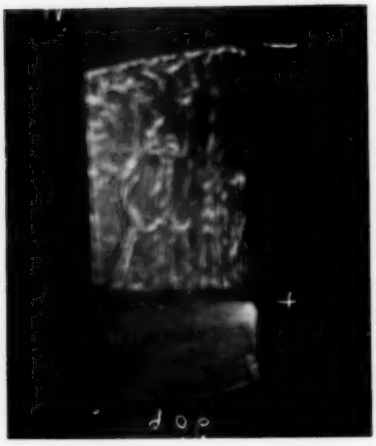
No. 32



No. 33

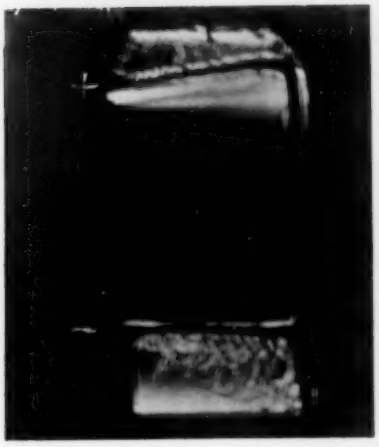


PLATE I. RAMSEY.

NEW BOOKS.

An Introduction to the Mathematical Theory of Attraction. FRANCIS A. TARLETON. Pp. xi+290. New York, Longmans, Green & Co., 1899.

The mathematical treatment of the theory of attraction from the point of view from which it has been actually developed, that of direct action at a distance, is necessarily of great intrinsic interest to the mathematician; but its prime importance to the mathematical physicist is due to the fact that the mathematical analysis and the actual body of formulæ which owed their origin to the old theory have proved to be applicable not only to electrostatics, but, with very little modification, to such apparent dissimilar subjects as the flow of fluids (including heat and electricity) and stress and strain in elastic solids.

Now it is true that electrostatics can be treated in part from the point of view of action at a distance, but many of the most important phenomena depend upon the condition of the intervening medium, the so-called "field"; and in fluid flow and elasticity what corresponds mathematically to the "field" is the direct object of study.

The Newtonian law of gravitation is so hammered into the schoolboy from his earliest days that when he comes to the systematic study of the theory of attraction the idea of action at a distance seems to him entirely natural and simple in spite of its philosophical difficulties, and on this account our author in his laudable endeavor to smooth the path of the student is undoubtedly right in approaching his subject from this side; but after the ground has once been broken too much emphasis cannot be laid on the study of the condition of the intervening medium, that is, of the field of force due to the presence of the attracting or repelling masses. It seems to me that the main respects in which the book under review is open to adverse criticism are the lack of this emphasis, the scarcity of problems where numerical results are demanded, and the absence of any allusion to vectors and vector-functions.

As it must always seem ungracious to find fault with an author who has given us much, because he has not seen fit to give us more, I hasten to speak of some of the many merits of the book. The definitions are clear and precise and not too numerous; the proofs are unusually direct and simple; the propositions are very well arranged, and, within the range to which the author has limited himself, include about all that even the advanced student is likely to need; and the problems are abundant even for an English treatise, and are well selected and instructive.

The consistent treatment of the "columnar" cases, as if there were a uniplanar distribution of mass acting inversely as the distance, is a prominent feature of the treatise, and one for which much can be said.

The book is certainly one from which the student who is thrown on his own resources can obtain a competent knowledge of the theory of attraction without waste of labor or loss of interest, and this is no small praise, especially, as in the words of the preface "It is a book for students not for professors." The skillful professor for whom it is not intended could perhaps use with greater effect on his class a judicious combination of Routh's Statics, Minchin's Statics, and Webster's Electricity and Magnetism.

W. E. BYERLY.

CAMBRIDGE, July 10, 1899.

Stars and Telescopes. A Handbook of Popular Astronomy. By DAVID B. TODD. Pp. xvi + 419. Boston, Little, Brown & Co. 1899.

In this volume Professor Todd has gathered together the most important data of the new astronomy in a form intelligible to every reader. The allotment of space to astrophysics is relatively much larger than in previous treatises on astronomy, and this is a feature which will render the volume useful to the student of physics as well as to the student of astronomy. The book is copiously illustrated. There are numerous reproductions of modern star photographs and spectra, together with pictures of the various types of apparatus used in astrophysical work. There is a great range of merit in these illustrations, some of which are extremely satisfactory while others show all the worst features of half-tone reproductions directly from the photograph. The list of references to the original sources with which each chapter closes is an admirable feature.

E. L. N.